Volume XXIV. *January, 1907.* *Number 1.*

THE

PHYSICAL REVIEW.

ON THE COEFFICENT OF EXPANSION OF FUSED QUARTZ.

By Howard D. Minchin.

THE increasing use of fused quartz in physical and chemical work and especially in optical problems renders the accurate knowledge of its physical properties very desirable. Its extremely small coefficient of expansion adapts it to investigations in which sudden changes of temperature are unavoidable and even greatly to be desired, while its transparency and high fusing point render it peculiarly suitable for the optical treatment of all problems involving wide ranges of temperature. The study of the thermal expansion of fused quartz has formed the subject of numerous recent investigations among which may be mentioned those of Le Chatelier,[1] Callendar,[2] and Holborn and Henning.[3]

Le Chatelier used a differential method, having two prisms of the same length, one of fused quartz and the other of porcelain. The latter was used as the standard, its coefficient of expansion having been determined by direct measurement. The two prisms were placed in a crucible of plumbago set in a bed of carbon which was heated to incandescence, and the expansions were measured by a cathetometer reading to 0.01 mm. The temperature was determined by means of an air thermometer. The mean coefficient of expansion of the fused quartz was found to be 70×10^{-8} between

[1] Comp. Rendus, 130, p. 1703, 1900.
[2] Chem. News, 83, p. 151, 1901.
[3] Ann. der Physik, 10, p. 446, 1903.

the temperatures of 0° and 1000° C. A contraction was reported as taking place at about 800° C.

Callendar used a rod of fused quartz about 40 cm. long, clamped at one end, and measured the expansion by means of a micrometer microscope reading to 0.001 mm., focussed upon the free end. The rod was heated by placing it in a platinum tube carrying an electric current. The expansion of the platinum tube was determined and the temperature to which the quartz was heated was computed from the coefficient of expansion of platinum. The mean coefficient of expansion of the fused quartz between room temperature and 1000° C. was found to be 59×10^{-8}. The expansion was found to be regular up to 1000° but from 1000° to 1400° C. it increased rapidly, and beyond 1400° a contraction took place.

Holborn and Henning used a rod of the material about 52 cm. long and observed the change in length by means of telescopes focussed upon marks cut near the ends of the rod. The rod was heated electrically[1] by placing it in a porcelain tube 80 cm. long mounted horizontally. Temperature measurements were made by means of a thermoelement, and the temperature of the rod was determined at nine different points throughout its length. Observations were made at room temperature, at 250°, 500°, 750°, and 1000° C. As a mean of fourteen determinations 54×10^{-8} is given as the coefficient of expansion.

The marked discrepancy in the results thus far obtained seemed to justify a redetermination of this important constant, with more delicate apparatus for measuring the expansion and especial devices for maintaining the temperature of the expanding solid both uniform and constant.

METHOD.

The method used in this investigation for measuring the coefficient of expansion is briefly as follows: A ring of the fused quartz about 1 cm. long is placed in an electrically heated oven and the expansion is determined by the displacement of interference fringes. The higher temperatures are determined by means of a thermoelement and the lower temperatures by means of mercury thermometers. The method of determining the expansion by the dis-

[1] Ann. der Physik, 2, p. 505, 1900.

placement of interference fringes is a modification of the method first employed by Fizeau.

The fused quartz system (Fig. 1) is arranged for the measurement of the expansion in the manner first devised by Pulfrich[1] and used by Reimerdes[2] and later by Randall.[3] The bed-plate *A* is of fused quartz 38.4 mm. in diameter and 10 mm. thick, and with its two faces ground approximately parallel. Its upper surface is plane polished, while the lower surface is left rough and ground in such a way as to leave three equidistant feet so that when the plate is mounted upon a level surface its upper surface is horizontal. The piece of fused quartz *Q*, whose coefficient of expansion was to be studied, is in the form of a ring approximately 9.9 mm. long, 31.8 mm. in external diameter, and 24.4 mm. internal diameter. This ring was made from a circular plate whose two surfaces have been ground and polished accurately plane parallel. From the center of this plate was cut a cylinder 24.4 mm. in diameter. Each end has been ground away so as to leave three equidistant feet as shown in the figure. The cover-plate *B*, also of fused quartz, is 7.5 mm. thick and 36.0 mm. in diameter. Its surfaces are plane polished and inclined to each other at an angle of about 20 minutes in order to avoid the disturbing effect due to the light reflected at the upper surface. A small plate *C*, not shown in the figure, made from the same material as the other pieces is approximately 19.8 mm. in diameter and about 0.2 mm. thick. Its upper surface is plane polished and its lower surface is rough and ground away so as to leave three feet similar to the arrangement of the bed-plate.

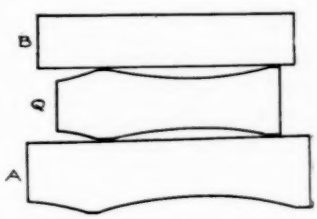

Fig. 1.

In arranging the parts preparatory to making a series of observations the plate *C* is placed upon the bed-plate *A* and the ring *Q* is then placed upon *A* symmetrically about *C*. The cover-plate *B* is next placed upon the ring *Q*. One of the feet of *C* was ground

[1] Zeitschr. für Krystall., 31, p. 372, 1899.
[2] Inaug. Diss., Jena, 1896.
[3] PHYS. REV., 20, p. 10, 1905.

off sufficiently to make the angle included between C and the lower surface of B of the proper size to give interference fringes of the desired width. For the purpose of measurement the cover-plate B has at the center of its lower surface a small fine circle and around this a number of concentric circles. The inner circle serves as a fixed point in the field of view from which measurements are made. Upon the upper surface of B is a fine mark cut parallel to the thin edge of the plate. This mark is to enable the operator to place the parts in the same relative position, each time the system is set up.

The fused quartz parts were made from material produced in the smelting works of the firm of Carl Zeiss, Jena, and the ring and optical surfaces were also made by Zeiss.

When the apparatus is clean and properly adjusted and illuminated by monochromatic light the eye will see the surface of the plate C crossed by a system of parallel interference fringes. When the illumination is produced by light of different colors a system of rainbow colored fringes can be observed. Each dark band of the fringe system represents a definite thickness of the air layer between B and C. Let λ be the wave-length of the light used, then the thickness of the air layer under any dark band differs from the thickness under the next dark band on either side by $\frac{1}{2}\lambda$. When the fused quartz system is heated the ring Q expands and the plates B and C are separated and the interference fringes move toward the thin edge of the included air layer. The number of dark bands passing under the small reference circle on B represents the change in the thickness of the air layer immediately under this circle and thus measures the expansion of the ring Q in terms of the wave-length of the light employed. The total expansion for any temperature interval $(t_2 - t_1)$ is $f \times \lambda/2$, where f is the number of dark bands passing under the reference circle for a temperature change from t_1 to t_2, and λ is the wave-length of light used. We then have the coefficient of expansion α, given by the equation

$$\alpha = \frac{f\frac{\lambda}{2}}{L(t_2 - t_1)},$$

where L is the effective length of the fused quartz expanding, that

is, the length of the ring Q, minus the length of the small plate C.

The spectral lines used for measurements were the mercury green ($\lambda = 546\ \mu\mu$) and the yellow lines of mercury ($\lambda = 578.8\ \mu\mu$ and $\lambda = 576.8\ \mu\mu$). The hydrogen red ($\lambda = 656.2\ \mu\mu$) was also used for some measurements but the intensity of illumination was not satisfactory and its use was abandoned.

Apparatus.

The interferometer employed was an Abbé-Fizeau instrument as modified and improved by Pulfrich, and constructed by Carl Zeiss, Jena. The same instrument was used by Randall,[1] who has given a full description with detailed directions for its manipulation in connection with his investigation upon crystalline quartz. As a source of light the ordinary H-form of Geissler tube containing hydrogen and vapor of mercury was used.

The Supporting System.

To avoid the presence of metal in the furnace the support for the quartz system was constructed as follows: Two rods FF (Fig. 2), of Berlin porcelain, about 50 cm. long, are clamped to a metal block E, by means of metal straps and held in position by screws. These rods carry at their lower ends a porcelain plate M. The block E, is made tapering in order to admit the interferometer tube between FF, and also as an aid in holding M in place. The rods FF, are notched at their lower ends to fit into slots cut in M as shown in the figure. This holds M sufficiently rigid to furnish a stable support for the optical system.

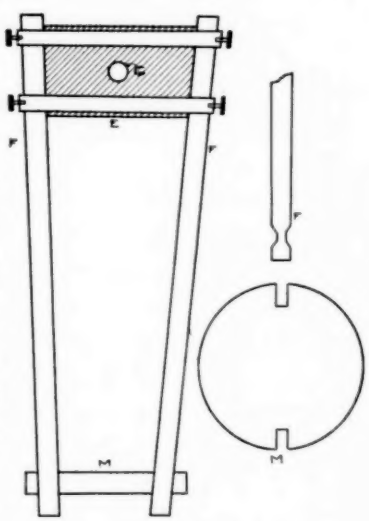

Fig. 2.

To mount the support a threaded hole G (Fig. 2), is made in the center of E, into which is screwed a thirteen millimeter steel rod.

[1] Loc. cit.

This rod is held by a right angled clamp to a larger rod attached rigidly to the pier. This method of mounting gives to the support two adjustments for levelling. It may be revolved on the rod attached to E in a plane at right angles to the axis of the interferometer tube, and also around the second rod in the plane of the axis of the interferometer tube. This gives sufficient freedom of movement to permit of accurate adjustment of the interference system.

THE ELECTRIC FURNACE.

The furnace consists of an unglazed porcelain battery jar 14.6 cm. inside length and 6.9 cm. inside diameter. A thin sheet of chemically pure asbestos paper was wound around this cylinder and then upon this two coils of rolled platinum wire were wound with the strands about 2 mm. apart. Fourteen feet of number 20 platinum wire was used. This was rolled so that its width was about twice its original diameter when its length was about 28 feet. The coils were wound separately so that either coil may be used alone, both coils may be used in parallel, or the two coils may be used in series. The plan of winding and the connections are shown in cross-section in Fig. 3. The resistance of each coil at room temperature is about 2.5 ohms.

The coils were covered with about a half inch coating of ganister made into a mortar. This material is a mixture of six parts of white sand and one part of clay ground together very fine. This was then covered by several layers of asbestos paper with small strips of asbestos between so as to keep the layers separated from each other for the purpose of lessening the radiation. The asbestos winding was carried about two inches above the porcelain cylinder. The whole was then packed in mineral wool, in a sheet-iron cylinder and mounted upon a table capable of being raised or lowered by

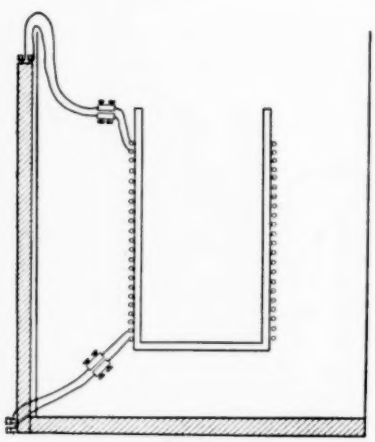

Fig. 3.

means of a screw actuated by a crank. This table was sufficiently rigid to prevent any lateral displacement of the oven, or jarring of the optical parts.

The cover was a porcelain plate similar to *M*, and split through the middle so that it could be put in place when the supporting system was adjusted in the furnace. Openings were made in it for the thermometers and thermoelements and also to admit the light. The arrangement of the cover is shown in Fig. 4, where *A* is the central opening about one inch in diameter to admit the light, *bb* are openings for the thermometers or thermoelements, and *cc* are the openings for the supporting rods *FF*.

In order to prevent radiation through *A* and yet not cut off the light a series of air chambers was built up. The opening *A* was

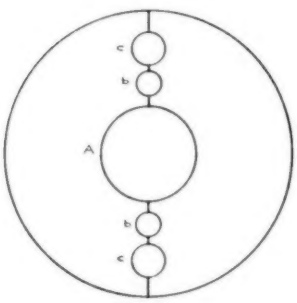

Fig. 4.

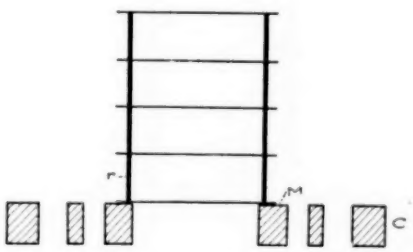

Fig. 5.

covered with a thin sheet of mica, then a collar or ring of glass, cut from a glass tube about one inch in diameter, was placed on the mica and over the opening, this ring was covered by a second sheet of mica, another glass collar added and another covering of mica. In this way four air chambers were built up, which served as an excellent check to radiation and did not noticeably diminish the illumination of the fringe system. A cross-section of the arrangement of the air chambers is shown in Fig. 5, where *C* is the cover, *M* the mica sheets and *r* the glass collars.

The effectiveness of the heat insulation was shown by the fact that the sheet-iron cylinder in which the furnace was packed showed but little rise in temperature when the furnace was heated up to 1000° C. Two thermometers were hung above the furnace, one close to the supports *FF* and within a few centimeters of the inte-

rior of the furnace, near the air chambers above *A*, the other just outside of the asbestos packing, and these showed temperatures but a few degrees above that of the room in each case. The small mass of the furnace renders it possible to heat up very quickly and at the same time allows the temperature of the interior to follow very closely every change in the heating current. The temperature can be held constant, to the full limit of the accuracy of the temperature measurements, for hours at a time. A current of 5 amperes is sufficient to heat up to 1000° C. in about two hours. In order to test the uniformity of the temperature within the heated space a series of temperature determinations was made

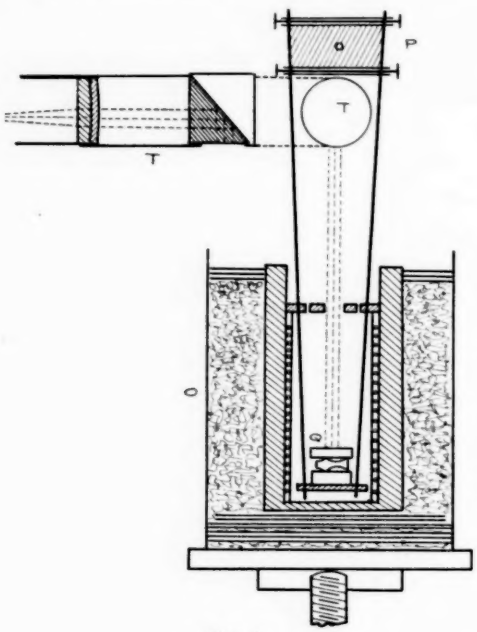

Fig. 6.

in the different regions of the furnace. Two thermoelements were used and so adjusted that the temperatures of two separate regions of the furnace were determined at the same time. The temperature was found to be constant to within 0°.5 throughout the whole interior, no variation being detected until the one element was brought within a centimeter of the top of the furnace and this variation disappeared when the cover and insulating material had been properly adjusted.

The apparatus was set up in a basement room of the Physical Laboratory of the University of Michigan. A brick pier served as a support for the interferometer and the supporting system. The electric oven and other devices were mounted upon the asphalt floor. In Fig. 6 is shown a vertical section of the end of the interferometer tube T, the electric oven O, the supporting system P and the quartz system Q when adjusted for work.

During the first part of the investigation the direct current, at 220 volts pressure, from the university lighting plant was used. Later it became necessary to use current from the storage battery for heating. This battery gave but 70 volts, yet owing to the low resistance of the coils of the furnace sufficient current was available for heating up to 1000° C. or more, while the extreme steadiness of the current proved to be a great advantage when it was necessary to keep the temperature constant at any point above the temperature of the room.

Table I. gives an idea of the performance of the furnace and its condition as regards uniformity and efficiency for the various temperature intervals worked over.

TABLE I.

Temperature Interval Worked Over.	Mean Current Used to Heat Up.	Time Required to Heat Up.		Current Required to Hold Temperature Constant.	Time During Which the Temperature was Held Constant.	
	Amperes.	Hours.	Min.	Amperes.	Hours.	Min.
Room temperature to 300°	3.0	1	05	2.4 to 2.5	2	20
" " " 400	3.0	1	10	3.2	2	30
" " " 500	3.5	1	20	3.3 to 3.4	2	50
" " " 600	5.0	1	16	3.6 to 3.8	2	00
" " " 700	5.0	1	30	3.9	2	45
" " " 800	5.0	1	50	4.6 to 4.8	2	20
" " " 900	5.0	2	00	4.5 to 4.6	2	00

In calibrating the thermoelements mentioned above, the furnace was heated up to 1350° C. and it was later heated up to 1200° C. on a trial test for the time required to heat up. For this test 5.5 amperes were used and the time required to reach 1200° C. was two hours and ten minutes.

Thermometers.

Four thermometers were used. For room temperatures a Peters and Rost thermometer reading to 60° C. and calibrated in the physical laboratory was used. For temperatures up to 200° C. two standard thermometers, made by Haak of Jena, were used, the one graduated from — 20° C. to 105° C., the other from 90° C. to 210° C. These were calibrated at the Reichsanstalt. The fourth thermometer is graduated in degrees, having a short scale at 0° C. and after an enlargement of the bore the graduation extends from 195° C. to 550° C. This thermometer was also calibrated at the Reichsanstalt. For temperatures between 300° C. and 1000° C. a platinum platinum-rhodium thermoelement was used. This element was certified by the Reichsanstalt. As a check on the latter a platinum platinum-iridium thermoelement, made by myself and calibrated in the physical laboratory, was used. As a further check both these thermoelements were compared with a platinum platinum-rhodium element, certified by the Reichsanstalt, and belonging to Professor E. D. Campbell, director of the chemical laboratory.

In measuring the temperature by means of the thermoelement the method used was the compensation method described by Lindeck and Rothe.[1] The apparatus was made by Siemens and Halske according to specifications of the Reichsanstalt.

The Spherometer.

The spherometer used in measuring the fused quartz ring and plates was one made by the Geneva Society and reads to 0.001 mm. The dimensions of the different parts of the fused quartz used in the computations were obtained by taking the mean of several series of readings. The length of Q is the mean of thirty readings, and the length of C is the mean of twenty-four readings.

Adjustment of the Apparatus.

The adjustment of the interferometer and the Geissler tube was made according to the method described by Randall.[2] The support

[1] Zeitschr. für Instr., 20, p. 285, 1900.
[2] Loc. cit.

P (Figs. 2 and 6) was mounted independently upon rods clamped to the pier and so arranged that it could be readily adjusted for the proper level. The thermoelement K (Fig. 7), was fastened to one of the supporting rods F, so that it passed through one of the openings of the cover of the furnace. Its junction J, was placed within about two millimeters of the ring Q, and between A and B as indicated in the figure.

In the adjustment of the system great care was necessary to avoid the presence of dust or lint between the surfaces at points where contact was desired, therefore each piece was thoroughly cleaned before being set in place. Plate A was placed centrally upon M of the support, C was placed in the center of A, the ring Q was then placed symmetrically around C, and the plate B placed on Q with the circles down. The support was then levelled and the optical system adjusted until interference fringes were obtained. The different pieces were marked to aid in placing them in the same relative position at each mounting of the system. When the fringes were erect and sufficiently bright readings were made upon two adjacent dark bands to determine the width of the fringes. To insure against the presence of dust or foreign particles between the surfaces in contact, the fused quartz system was taken down and remounted several times, the width of the fringes being determined each time. When several successive determinations gave the same band width it was assumed that the apparatus was in proper adjustment for work. The reference circle was then adjusted so that it was in the center of the field in order that any rectification of the fringes should still leave them symmetrically placed in the field.

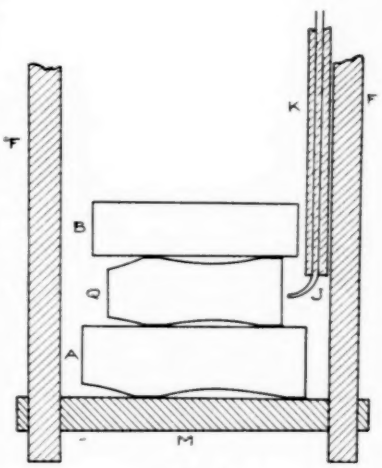

Fig. 7.

The furnace was then raised until the fused quartz system was near the bottom and symmetrically placed in the interior, the cover

C, was then put in place, the air chambers built over the opening *A*, and the space around these chambers packed with asbestos up to the asbestos winding on the furnace. For the lower temperatures a thermometer was introduced in the second opening *b*, and for the higher temperatures the second thermoelement was used in a manner similar to the one already described. The apparatus was allowed to stand over night in order to allow it to acquire a stationary temperature. The position of the fringes was read and the temperature and barometric pressure determined. The current was then turned on and the system heated up to the desired temperature. The current was then adjusted so as to maintain this temperature constant and micrometer readings were made upon some one of the dark bands in the field of view. The temperature was kept constant and at intervals of about 20 minutes the position of the dark band selected was again determined. After the temperature had been held constant for about an hour the position of the band did not change. This indicated that the system had acquired a stationary temperature. The final readings on the bands were taken after the temperature had been held constant for a period of not less than two hours. In all micrometer readings made upon the fringes a mean of ten or more readings was taken. During the heating of the quartz the number of dark bands passing the reference circle were counted. When the readings at the desired temperature had been made the current was shut off and the system was allowed to cool to room temperature and another set of readings made. Thus for each temperature interval worked over, two separate determinations were made, one from the lower temperature to the higher and a second from the higher to the lower temperature. In this way separate determinations were made over the temperature intervals between room temperature and each of the temperatures 200°, 300°, 400°, 500°, 600°, 700°, 800°, 900° and 950° C. After each of the series of readings 1, 2, 5 and 6 given in Table II., the quartz was removed from the furnace, taken down, remounted and the furnace again adjusted for the next series of readings. The quartz pieces were all carefully measured after the heating was completed and their lengths were found to be the same as at the beginning.

Two methods were used for determining the number of fringes displaced, the one by direct observation, the other by computation.

By means of the micrometer attached to the eye-piece of the interferometer the exact position of the bands was determined and then the number of whole bands passing the reference circle was counted while the system was being heated up to the desired temperature. To this whole number was added the fraction of a band by which the last dark band had passed the reference circle, and from this was subtracted the fraction of a band by which the first dark band was past when the counting began. The total fringe displacement was then given by the formula

$$f = M + \partial_{t_2} - \partial_{t_1},$$

where M represents the number of whole bands observed and ∂_{t_2} and ∂_{t_1} the fractions of a band at temperatures t_2 and t_1. These quantities were determined from the micrometer readings. The heating and the expansion were so regular that once having determined the time of passage of a dark band it was an easy matter to check up the result.

The method by computation is that first described by Abbé.[1]

As a change in the temperature and pressure results in a change in the index of refraction of the air layer between the reflecting surfaces, a correction was made upon the observed number of fringes displaced. The correction was computed by the following formula given by Pulfrich:[2]

$$K = d(t_2 - t_1)\frac{b_1}{760}\cdot\frac{1}{1+at_1}\cdot\frac{1}{1+at_2}\left[2\frac{(N-1)a}{\lambda}\right] + d(b_2 - b_1)\frac{1}{1+at_2}\left[2\frac{N-1}{\lambda}\cdot\frac{1}{760}\right]$$

in which K represents the correction, d the thickness of the air

[1] Wied. Ann., 38, p. 473, 1889.

[2] Zeitschr. für Instr., 13, p. 455, 1893. While the relation here assumed to exist between the index of refraction of a gas and its temperature and pressure, is known to hold for temperatures up to 100° C., no data, so far as is known to the writer, exist for the behavior of a gas at such temperatures as are reached in this work. An investigation of the validity of this correction for temperatures between 100° and 900° C., is being made by Dr. Randall.

layer $= Q - C$ (Fig. 1), b_1 the barometric pressure observed at the lower temperature t_1, b_2 the barometric pressure at the higher temperature t_2, α the coefficient of expansion of air, N the index of refraction of air under standard conditions and λ the wave length of light used.

THE DEGREE OF ACCURACY.

The formula for the coefficient of expansion

$$\alpha = \frac{f\frac{\lambda}{2}}{L(t_2 - t_1)}$$

shows that α is dependent upon the variables f, L, t_2, and t_1. In the expression $f = M + \partial_{t_2} - \partial_{t_1}$ the ∂'s could be determined with an error affecting f by $\pm$ 0.02 of a fringe and the resulting error in the value of α for the larger temperature intervals is $\pm$ 0.1 $\times$ 10^{-8} and for the smaller temperature intervals it is $\pm$ 0.5 $\times$ 10^{-8}. The length of L could be determined to within $\pm$ 0.001 mm. and the error in α due to this error is 0.01 $\times$ 10^{-8}. The temperature measurements made with the thermometers could be determined with an error of $\pm$ 0.1° C. With the thermoelement the temperature could be determined with an error of $\pm$ 0°.5 at the lower temperatures and $\pm$ 2° at the higher temperatures. The error in α resulting from the measurement of the temperature intervals is $\pm$ 0.1 $\times$ 10^{-8} and $\pm$ 1.1 $\times$ 10^{-8} respectively. The total effect of these errors upon the final result is given by the equation

$$E = \sqrt{E_f^2 + E_L^2 + E_t^2}$$

where E_f, E_L, and E_t represent the error in the measurement of the number of bands, the length of the ring, and the temperature interval, respectively. For the shorter temperature intervals at the higher temperatures, this amounts to 1.6 $\times$ 10^{-8} and for the longer intervals it is 0.5 $\times$ 10^{-8}.

The series of readings in Table II. were made for the temperature intervals indicated.

After the above series of readings were made the apparatus was dismantled and the quartz system, the furnace, and the thermoele-

TABLE II.

Date.	Series.	Temperature Interval Worked Over. (1)	(2)
1905, Sept. 2	1	Room temperature to 200°	Back to room temperature.
" 7		" " " 300	" " " "
" 8		" " " 400	" " " "
" 9		" " " 500	" " " "
" 10		" " " 600	" " " "
" 11		" " " 700	" " " "
" 12		" " " 800	" " " "
" 13		" " " 900	" " " "
" 13		" " " 950	" " " "
" 14	2	" " " 600	" " " "
" 14	3	" " " 800	" " " "
" 15	4	" " " 300	" " " "
" 15		300° " " 400	
" 15		400 " " 500	
" 15		500 " " 600	
" 15		600 " " 700	Back to room temperature.
" 16	5	Room temperature to 800°	
" 16		800° " " 900	
" 16		900 " " 950	

ments were taken to the University of Rochester where the apparatus was again set up. A new Abbé-Fizeau interferometer belonging to the University of Rochester was used, and for measuring the temperature an Otto Wollf potentiometer was used in connection with the thermoelements in place of the compensation device of Siemens and Halske. The series of readings given in Table III. were then made.

TABLE III.

Date.	Series.	Temperature Interval Worked Over. (1)	(2)
1905.			
Nov. 8	6	Room temperature to 300°	Back to room temperature.
" 10		" " " 500	" " "
" 11		" " " 700	" " "
" 22		" " " 900	" " "
Dec. 5	7	" " " 200	
" 18	8	200° to 400	
" 19		400 to 600	
1906.			
Jan. 16		600 to 700	
" 18		700 to 800	

EXAMPLE OF A COMPLETE DETERMINATION.

September 7, 1905.

Length of fused quartz ring, 9.9009 mm. Effective length of fused quartz expanding, 7.9513 mm.

Length of fused quartz cylinder, 1.9496 mm. Thickness of air layer, 7.9513 mm.

Computation for one set of readings:

$t_1 = 18.4$ C. , $b_1 = 742.0$ mm.

$t_2 = 300°$ C. , $b_2 = 742.6$ mm.

$\delta_{t_1} = 0.2736$, $\delta_{t_2} = 0.3981$ mm.

M observed $= 3$, $\lambda = 0.000546$ mm.

$f = 3 + 0.398 - 0.274 = 3.124$.

$K = 0.385$.

$f_0 = 3.124 + 0.385 = 3.509$.

f_0 = number of bands when correction is applied.

$$a = \frac{f_0^2/2}{L(t_2 - t_1)} = 43 \times 10^{-8}.$$

RESULTS.

Table IV. contains the data obtained in the physical laboratory of the University of Michigan. Table V. contains the data obtained in the physical laboratory of the University of Rochester.

TABLE IV.

Series.	Temperature Interval Worked Over.									
	Lower to Higher.				a		Higher to Lower.			a
1	Room temperature	to	200°		43.2×10^{-8}		Back to room temperature.			43.3×10^{-8}
	"	"	"	300	43.0	"	"	"	"	43.2 "
	"	"	"	400	44.0	"	"	"	"	44.5 "
	"	"	"	500	46.0	"	"	"	"	45.7 "
	"	"	"	600	44.0	"	"	"	"	44.8 "
	"	"	"	700	44.0	"	"	"	"	44.1 "
	"	"	"	800	46.0	"	"	"	"	45.8 "
	"	"	"	900	43.0	"	"	"	"	44.0 "
	"	"	"	950	44.0	"	"	"	"	44.2 "
2	"	"	"	600	46.0	"	"	"	"	45.7 "
3	"	"	"	800	46.0	"	"	"	"	45.8 "
4	"	"	"	300	44.0	"				
	300°	"	"	400	44.0	"				
	400	"	"	500	46.0	"				
	500	"	"	600	45.0	"				
	600	"	"	700	45.0	"				
5	Room temperature		"	800	46.0	"				
	800°	"	"	900	44.0	"				
	900	"	"	950	45.0	"				

TABLE V.

Series.	Temperature Interval Worked Over.									
	Lower to Higher.			α		Higher to Lower.			α	
6	Room temperature	to	200°	44.0×10^{-5}		Back to room temperature.			44.5×10^{-5}	
	"	"	" 500	46.0	"	"	"	"	45.4	"
	"	"	" 700	44.8	"	"	"	"	45.2	"
	"	"	" 900	45.0	"	"	"	"	45.1	"
	"	"	" 200	43.0	"					
7	200°	"	" 400	45.0	"					
8	400	"	" 600	44.5	"					
	600	"	" 700	45.0	"					
	700	"	" 800	46.0	"					

CONDITIONS FOR OBSERVATIONS.

At about 400° C. the interior of the furnace began to appear bright and at about 500° C. it gave a reddish tint. This light, however, did not interfere with the readings upon the interference fringes. Between 700° C. and 800° C. a band of reddish light emitted by the fused quartz appeared in the telescope of the interferometer in the neighborhood of the hydrogen red of the Geissler tube. At about 825° C. this light became so bright that it annulled the hydrogen red in the field, and above 950° C. the intensity of the light from the fused quartz was so great that further readings were impossible. The colors used in the interference phenomenon were the yellow and the green lines of mercury, and up to 950° C. the brilliancy and sharpness of the fringes due to these lines were as marked as at the lower temperatures. Even at this high temperature there was no wandering or quivering of the fringes, and readings could be taken as readily as at the lower temperatures. This was due to the freedom from air currents and to the perfect insulation of the furnace. In so far as the writer is aware interference fringes have not been previously used for measurements at temperatures above 500° C.

In the construction of the interferometer the light is analyzed by a direct vision prism train in the eye-piece, and it is possible that some modification of this set of prisms might render it possible to extend the temperature limit at which the fringes could be read to 1100° C. or 1200° C. The use of some element in the Geissler tube which would give brilliant lines in the blue or violet would certainly extend this range.

COMPARISON OF RESULTS WITH THOSE OF OTHER OBSERVERS.

The results obtained in the investigations referred to in the introduction are given below together with that obtained by the writer.

	a
Le Chatelier	50×10^{-8},
Callendar	59×10^{-8},
Holborn and Henning	54×10^{-8},
Minchin	45×10^{-8}.

It is seen that the result obtained by the writer is considerably below the other results. Le Chatelier in his work used the differential method, using porcelain as his standard. He found certain irregularities in the expansion of the fused quartz, but Callendar thinks it probable that this was due to the irregularities inherent in the expansion of porcelain. Shenstone [1] says the fused quartz used by Le Chatelier was probably impure, and Le Chatelier himself expresses doubt as to its purity.

Callendar placed a rod of the fused quartz in a platinum tube and clamped both at one end and read the expansion by means of a micrometer microscope reading to 0.001 mm. His method of determining temperatures was, to say the least, indirect and liable to error.

The value $a = 54 \times 10^{-8}$, given by Messrs. Holborn and Henning as the result of their measurements, was a mean value obtained from several different ranges of temperature. The following table contains, in the first two columns the data given by Holborn and Henning,[2] to which has been added in the third column the corresponding value of a computed by the writer.

The effective length of the fused quartz expanding was 486.9 mm.

As will be noted from the table, the individual values of a vary considerably, and while several of these values are comparable to the result obtained in this investigation, still the differences between individual values of the series are sufficiently large to warrant some consideration of the method employed.

The method used by Messrs. Holborn and Henning, while offering the seeming advantage of a great length of the expanding substance, was weak in that it failed to secure uniform temperature

[1] Nature, 64, p. 65, 1901.

[2] Ann. der Physik, 10, p. 447, 1903.

throughout the length of the rod, the temperature of the ends being ten per cent. lower than that of the middle.[1] It was also found necessary to correct for the expansion of the supports of the reading microscopes and it seems possible that the method employed might involve other errors due to expansion, which were not entirely eliminated by the foregoing correction. In discussing the rather wide variation between their individual results, they suggest that this may possibly be due to the irregular form of the fused quartz rod under examination.[2] By means of their apparatus Messrs. Holborn and Henning were able to measure elongations to 0.001 mm., which in a rod of 50 cm. length would amount to 1 part in 500,000.

TABLE VI.

Temperature Interval Worked Over.	Expansion for Interval in μ.	α	Temperature Interval Worked Over.	Expansion for Interval in μ.	α
17° to 250°	54.0	47.6×10^{-8}	500° to 750°	68.0	55.9×10^{-8}
	57.5	50.7 "		62.0	50.9 "
				60.0	49.3 "
	54.0	47.6 "		62.5	51.3 "
	52.0	45.8 "	16° to 750°	192.5	53.9 "
250° to 500°	79.5	65.3 "	750° to 1000°	66.0	54.2 "
	74.0	60.8 "		61.0	50.1 "
	77.0	63.3 "			

The method and the apparatus employed in the present investigation seem to justify confidence in the results obtained for the following important reasons.

(*a*) *Uniformity of Temperature Throughout the Expanding Body.* — As has been pointed out, the temperature of the interior of the electric furnace did not vary by as much as 0°.5 throughout a range of about 14 cm., and the length of the expanding quartz, being approximately 1 cm., the error from inequalities of temperature in its different parts may be considered as eliminated.

(*b*) *Constancy of Temperature During Measurements.* —The temperature of the furnace and its contents was held constant during the measurements or at least the variations of temperature were

[1] Ann. der Physik, 2, p. 507, 1900.

[2] Ibid., 10, p. 447, 1903.

smaller than could be detected by means of the apparatus employed, *i. e.*, the compensation apparatus, furnished by Siemens and Halske. The use of the current from the storage battery contributed greatly to this result.

(*c*) *Uniformity and Homogeneity of the Quartz Specimen Examined.* — The quartz ring employed, received from the smelting works of the "Zeiss Fabrik" may safely be assumed to be an excellent sample of pure fused quartz, while its small length and the symmetry of its parts render errors from any want of symmetry, or lack of homogeneity extremely unlikely.

(*d*) *Close Agreement Between Temperature Measured and Actual Temperature of the Quartz Ring.* — The junction of the thermoelement was placed within two millimeters of the surface of the quartz ring and since the variation of temperature in the interior of the furnace was practically *nil*, and since the temperature of the junction was constant both before and during the measurements, it may be assumed that the indicated temperature was very accurately that of the expanding quartz.

(*e*) *Variety of Temperature Ranges and of Conditions of Measurement.* — No pains were spared to make the variety of temperature intervals over which the expansion could be measured as great as possible, in order to detect any variation in the rate of expansion of the fused quartz within that limit, if such variation existed. Also the repetition of the measurements, in another laboratory, and under new conditions, and with new instruments is thought to give added value to the result obtained.

(*f*) *Delicacy of Measurements of Elongation.* — With the system as finally arranged for measurements, the fringe width was equivalent to 100 divisions of the divided head of the micrometer, for this rendered it possible to measure displacements to one two-hundredth of a wave-length. Hence elongations of double this amount, or 0.01 of a wave-length of the light employed, could be measured with ease. This gives, in the case of the yellow light from mercury vapor, the possibility of measuring elongations of the order of $0.000578 \times 0.01 = 0.000005$ mm., and this when used in connection with a length of 7.9 mm. of the expanding substance, amounts to one part in 1,500,000.

Summary of Results.

I. In this investigation it has been shown that interference methods are applicable to the measurement of minute lengths up to 950° C. when the fringes are produced between surfaces of fused quartz; and that up to this temperature the clearness and the brilliancy of the fringes are as great as at the lower temperatures.

II. The expansion of fused quartz is uniform from room temperature to the highest temperature observed. No change in the expansion, either as an increase or a sudden decrease, as was reported by Le Chatelier, was observed.

III. No after effects due to the heating were observed.

IV. The mean value of the coefficient of expansion of fused quartz, as deduced from 43 determinations, is

$$a = 44.9 \times 10^{-8}.$$

In conclusion the writer desires to express his gratitude to Professor Reed, under whose immediate direction this investigation was pursued, for the many suggestions offered, the kindly interest taken during the progress of the work, and for the generous loan of apparatus with which to pursue to completion the work at the University of Rochester. Thanks are also due to Dr. H. M. Randall for valuable suggestion and assistance in overcoming experimental difficulties.

Physical Laboratory, University of Michigan,
Ann Arbor, August 10, 1906.

ON THE MAGNETIC SUSCEPTIBILITY AND TEMPERATURE COEFFICIENTS OF $CuSO_4$ AND $MgSO_4$ SOLUTIONS.

BY CLARENCE K. STUDLEY.

I HAVE made some relative determinations on the solutions of the above named salts by the balance method as used by Professor Stearns in his determination of the magnetic susceptibility of water,[1] and with practically the same apparatus used by him.

The apparatus consists of a very sensitive non-magnetic balance of a special type designed by Helmholtz. This was, of course, enclosed in a glass case and the whole surrounded on all but one side by a zinc box to shield it from such external agencies as light, etc. The open side of the zinc box is provided with a black curtain, which is drawn over the opening when an observation is to be made. A glass tube passes up through a hole in the bottom of the balance case and connects it with the wooden box, *K*, into which the pole pieces, *PP*, of the large electro-magnet, *M*, project. This being almost airtight the apparatus is very effectively protected from external air currents. To the bottom of the balance-pan, *N*, is attached a silk cord which is practically inelastic for small weights so that the bottom of the tube, *T*, is at a constant height when the balance is in equilibrium. This cord passes down through the tube, *Q*, and terminates in a hook made of copper wire, which is inserted into the eyelet in the upper end of the thermometer, *H*. The tube, *T*, which contains the solution is fitted with a rubber cork, *C*, which is perforated so as to allow the thermometer to be passed through it and into the solution. By this means the tube, *T*, is suspended between the pole-pieces, *PP*. The pole-pieces are held apart a distance of 1.6 cm. by a brass block, *V*, which is hollowed out in the center so as to allow the tube, *T*, to pass below the center of the magnet pole. The box, *K*, is fitted with a slide door, *L* (which has a glass

[1] H. D. Stearns, PHYS. REV., Vol. XVI., No. 1, January, 1902.

window, *W*), which enables one to read the thermometer without opening the box. The electro-magnet rests on a solid bench, *X*, while the balance is supported by a solid plank whose ends, *AA*, rest on masonry piers. At the center of the balance-beam is a mirror

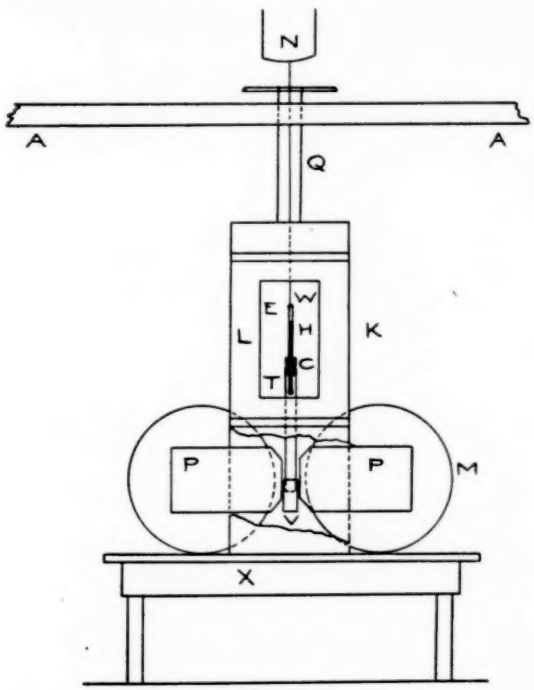

Fig. 1.

which reflects a scale into a reading telescope. The scale and telescope are at a distance of 1.5 meters. By this means it is possible to weigh accurately to $\frac{1}{1000}$ of a milligram with a 20 milligram rider.

The magnetic susceptibility (K) is given by the following formula which may be easily derived so it is not deemed necessary to give the theory at this time:

$$K = (2gp/H^2q).$$

Where (g) is the acceleration of gravity, (p) the attractive force in grams exerted by the magnet upon the cylinder in the direction of its axis (repulsion being denoted by a (−) sign before the quantity), (q) is the cross-section of the liquid cylinder, and (H) is the horizontal component of the magnetic field.

Since only a relative determination is desired we have only to measure the attraction (p) with a given tube and constant current. The other quantities remain the same.

I have used the susceptibility of water as $-.73.10^6$ which is the value obtained by Professor Stearns. The reason for my selection is not only because it was determined under the same conditions as those under which I have been working but also because since this is the mean value of the determinations made by the different investigators as shown by the following table I consider it the best determination yet made on water.

TABLE I.

Observer.	K.10^6.	Observer.	K.10^6.
Quincke.[1]	−.84	DuBois.[1]	−.86
Henrichsen.[2]	−.75	Curie.[3]	−.79
Townsend.[4]	−.77	Königsberger.[5]	−.80
Jäger and Meyer.[6]	−.66	Faraday.[7]	−.69
Becquerel.[7]	−.63	Wahner.[7]	−.536
BuBois.[7]	−.837	Stearns.[8]	−.73
			Mean value −.741

The salts used in these determinations were tested for iron but as no perceptible trace of it was found it is safe to say that the per cent. of iron, if there be any present, is so small as to be inappreciable.

The null point was taken both before and after the reading for the excited magnet, and if the variation of these two null points from the mean value is over one per cent. the reading is rejected. The residual magnetism was so slight that it may be easily neglected.

A single rider whose mass was about 20 mg. was used. As only a comparative determination is to be made it is not necessary to know its mass accurately.

[1] Wied. Ann., Vol. XXXV., p. 137, 1888.
[2] Wied. Ann., Vol. 45, p. 38, 1892.
[3] Journal de Physique, p. 206, 1895.
[4] Proc. Roy. Soc. London, LX., p, 186, 1896–7.
[5] Wied. Ann., Vol. 66, p. 698, 1898; Drude's Ann., Vol. VI., p. 506, 1901.
[6] Wied. Ann., Vol. LXVII., p. 712, 1899; Drude's Ann., Vol. VI., p. 870, 1901.
[7] Pogg. Ann., Vol. XXXV.
[8] PHYS. REV., Vol. XVI., No. 1, January, 1903.

The water used in making the solution was distilled from rain water caught in a glass bottle after copious showers had cleansed the tiled roof.

Readings were taken only every half hour so as to be sure that the solution was in a stable condition.

I have given one set of data in full so as to give some idea of the various features of the work. In this I have used the following notation :

C, the current in the electromagnet.

Rm, the number of scale divisions the rider has been moved along the balance arm from the position with zero current in the electromagnet to the position with (*C*) amperes current in the magnet coil.

No, null point with zero current in the magnet.

Nt, null point with current in the magnet.

Ni, null point after the current has been turned off.

T, the temperature registered by the thermometer (*H*). (See Fig. 1.)

p, the attraction exerted by the magnet on the tube (*T*) and contents.

4.53 *Per Cent.* $CuSO_4$ *Solution.*

C	*Rm*	*No*	*Nt*	*Ni*	*T*	p
10	2.5	26.7	29.8	26.6	16.7	−.01044
10	2.5	26.4	31.3	26.9	17.0	−.01065
10	2.5	26.2	31.3	26.8	17.3	−.01065
10	2.5	27.7	31.6	27.7	18.0	−.01051
10	2.5	31.5	36.8	31.8	19.0	−.01065
10	2.5	31.2	36.4	31.2	19.6	−.01057
10	2.5	32.6	39.4	32.8	19.9	−.01086
10	2.8	32.0	34.0	32.1	20.5	−.01082
10	2.8	31.9	34.1	32.2	20.5	−.01084

From the curves for empty tubes (I.) and (II.), Fig. 2, it will be seen that glass has a very high temperature coefficient. This causes a difference in the value of (p), for the tube, of .0004 per degree centigrade. Since the limit of possible error does not exceed 2.5 per cent. the variations in the above curves could not be due to this cause.

The curves for the 4.53, 7.16 and the 8.94 per cent. $CuSO_4$ solutions, Fig. 3, lie so near the origin that a small error in taking the data would make a great variation in the final result. In the 7.16

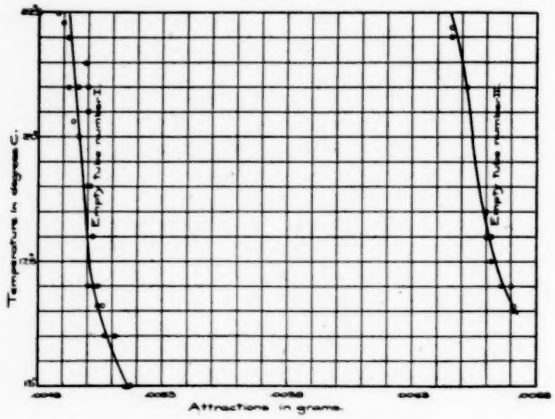

Fig. 2.

per cent. solution the greatest variation is 5 per cent. and in the 8.94 per cent. solution it is slightly over 3 per cent. but these are easily within the limit of experimental error. Hence I conclude that,

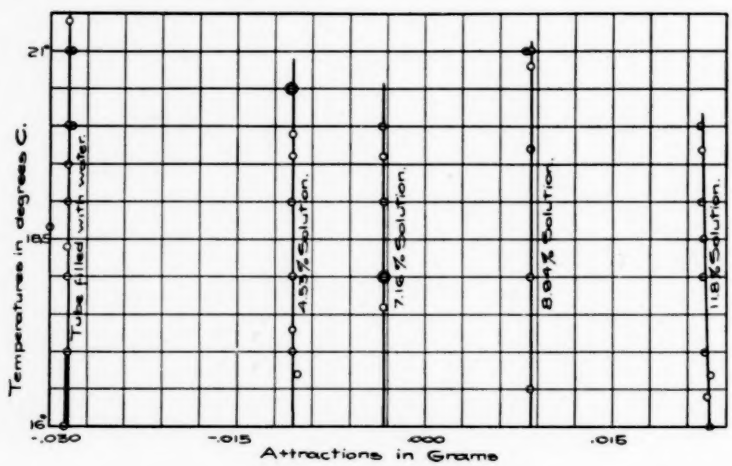

Fig. 3. $CuSO_4$ solutions.

between the limits of 16° and 21° C. there is no temperature coefficient in $CuSO_4$ solutions. Whether this is true or not for a wider range of temperatures remains to be seen.

Assuming $K \cdot 10^6$ to be $-.73$ for water, I have calculated the values of this quantity for each of the solutions used.

TABLE II.

Per Cent. Solution.	Specific Gravity.	$K \cdot 10^6$ (Measured).	K' (Calculated).	$K \cdot 10^6$ (Calculated).
7.16	1,071	$-.084$	.002	.002
11.8	1,117	.537	.476	.532
8.94	1,082	.212	.184	.199
4.53	1,032	$-.270$	$-.266$	$-.275$

The specific magnetism (K') of $CuSO_4$ is given by the formula[1]:

$$K' = (10.4)(P/100) - .80(1 - (P/100)).^2$$

Where P, is the per cent. of water-free salt in the solution, and $K' = K/s$ where K, is the magnetic susceptibility and s, the specific gravity of the solution.

The above computations show a very good agreement except in the case of the 7.16 per cent. solution.

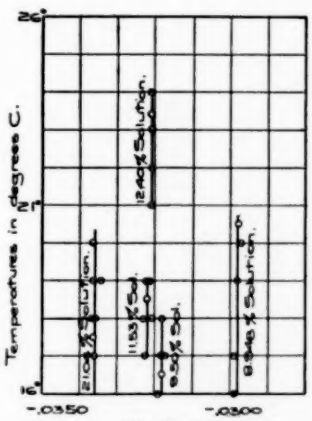

Fig. 4. $MgSO_4$ solutions.

$MgSO_4$ SOLUTIONS.

From the curves for the $MgSO_4$ solutions, Fig. 4, it can be easily seen that the greatest possible variation is much less than 2.5 per cent. (the probable error). Hence I conclude that, $MgSO_4$ solutions have no temperature coefficient for a range of temperatures from 16° to 21°C.

The specific magnetism of $MgSO_4$ is given by the formula:

$$K' = -.46(P/100) - .73(1 - (P/100)).$$

[1] Wied. Ann., Vol. LXVI., p. 698, 1898.

[2] Where $K \cdot 10^6$ is taken as $-.73$ the formula becomes:

$$K' = 9.49(P/100) - .73(1 - (P/100)).$$

TABLE III.

$MgSO_4$ Solutions.

Per Cent. Solution.	Specific Gravity.	$K \cdot 10^6$ (Measured).	K' (Calculated).	$K \cdot 10^6$ (Calculated).
9.48	1,089	−.698	−.704	−.767
21.04	1,200	−.823	−.672	−.806
12.40	1,118	−.786	−.696	−.778
11.53	1,109	−.789	−.698	−.774
8.95	1,084	−.780	−.706	−.765
4.73	1,038	−.765	−.717	−.744

The results show a very good agreement of experimental and calculated values except for the 9.48 per cent. solution. This is no doubt due to experimental error.

In reducing from the mirror scale to the balance arm scale I have used the relation, 1.5 divisions on the mirror scale equal .1 scale division on the balance arm scale.

What value there may be in this paper is due very largely to the aid and suggestions of Professors Sanford and Stearns, of the Physics Department.

STANFORD UNIVERSITY, 1905.

MAGNETIC SUSCEPTIBILITY OF MIXTURES OF SOLUTIONS.

By H. W. March.

THE following investigation of the magnetic susceptibility of mixtures of solutions of salts of copper, manganese, and aluminium was undertaken at the suggestion of Dr. E. P. Adams, to determine whether the susceptibility of such mixtures is an additive property.

A slight modification of Quincke's manometric method, as employed by Du Bois,[1] was used in measuring the susceptibility. A glass tube bent at right angles, one arm having a diameter of about 2.5 mm. and the other a diameter of about 25 mm., was mounted on a support with the long narrow arm passing between the pole pieces of a powerful electromagnet. The narrow tube was inclined at an angle of about 30° to the horizontal. Its support consisted of a board fastened to two standards embedded in a brick pier. A hole was cut in the board for the admission of the pole pieces. The tube was held in position on the board by two brass straps over the narrow arm through which it slipped, but into which it fitted snugly. There was thus no difficulty in removing the tube and returning it to its former position. A third brass strap over the wide arm of the tube kept it in place. The meniscus between the pole pieces was 25 cm. from the surface of the liquid in the wide arm.

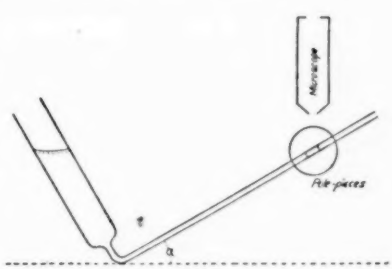

Fig. 1.

The pole pieces had the shape of a frustum of a cone. Their diameter was 3 cm. and they were 1 cm. apart during the experi-

[1] Wied. Ann., 35, p. 137.

ment. The field strength was measured by means of the change in the resistance of a bismuth spiral placed beside the meniscus. The spiral was made by Hartmann and Braun.

All measurements are relative, water being taken as the standard. Its susceptibility is taken to be -0.8×10^{-6}. As the observations on water and the solutions were made with nearly the same field strengths as indicated by the bismuth spiral, I think any inaccuracy in the calibration of the spiral was practically eliminated Since the measurements were referred to water it was not necessary to know the inclination of the tube nor the ratio of the cross sections of its arms. The displacement of the surface of the liquid was measured by means of a micrometer microscope mounted vertically over the meniscus in the narrow tube.

The susceptibility of a solution was computed by the formula whose derivation follows:

Let a_s = horizontal displacement of the meniscus of a solution.

H_s = corresponding field strength.

D_s = density of the solution.

a_w, H_w, D_w = corresponding quantities for water.

α = inclination of tube to horizon.

n = ratio of the cross section of the narrow arm to the cross section of the wide arm.

K_s = susceptibility of the solution.

If a_v denotes the difference in the heights of the two surfaces of the liquid under the action of the magnetic field, we have the relation,[1]

$$a_v g D = \frac{K}{2} H^2.$$

In this case, $a_v = a \sec \alpha (\sin \alpha + n)$.

[1] Du Bois, Wied. Ann., 35, p. 144.

We have then for the solution,

$$K_s = 2g \sec \alpha \, (\sin \alpha + n) D_s \frac{a_s}{H_s^2}.$$

And for water,

$$K_w = 2g \sec \alpha (\sin \alpha + n) D_w \frac{a_w}{H_w^2}.$$

$$\therefore \quad K_s = \frac{D_s}{D_w} \frac{\frac{a_s}{H_s^2}}{\frac{a_w}{H_w^2}} K_w = \frac{D_s}{D_w} \frac{\frac{a_s}{H_s^2}}{\frac{a_w}{H_w^2}} (-0.8) \times 10^{-6}.$$

On the assumption that the susceptibility is an additive property, the susceptibility of a mixture of solutions is computed by the formula,

$$K = M_1 K_1' + M_2 K_2'.$$

In this formula

M_1 = mass of first solution per cubic centimeter of the mixture.

K_1' = the specific susceptibility of the first solution, *i. e.*, the susceptibility per gram.

The susceptibility of each solution was found as the result of two sets of observations, with field strengths of approximately 8,000 C.G.S. units and 10,000 C.G.S. units respectively. A set of observations consisted of four separate determinations. Two determinations were made with the storage battery current direct and reversed. Then the connections of the battery used in measuring the resistance of the spiral were reversed to eliminate the effect of thermal currents, and two more determinations were made. Two zero readings were taken with the micrometer, one before closing the storage battery circuit, and one after opening it. I give as an example one of the sets of observations on water.

From a curve supplied with the spiral H is taken as the abscissa of a point whose ordinate Z is given by the formula.

$$Z = \frac{W_f - W_0}{W_0} [1 + 0.014(T - 18)].$$

In this case $H = 9{,}450$ and $(a/H^2)10^{11} = 13{,}800$. Frequent observations were made on water to determine the constancy of the

apparatus. The agreement of the values of a/H^2 was very good, showing that the tube maintained its constant inclination to the horizon.

	Initial Resistance. (W_0)	Final Resistance. (W_f)	T	Micrometer Readings.		
				r_0	r_f	Displacement.
D	18.92 ohms	26.53 ohms	21.5°	25.536 25.689	13.349	12.263
R	18.92	26.53	21.6	25.717 25.780	13.443	12.305
		Small Battery Reversed.				
D	18.90	26.53	21.7	25.794 25.810	13.418	12.384
R	18.90	26.53	21.7	25.788	13.423	12.346
	18.91	26.53	21.6	25.750		$a = 12.324$
	.08 (lead wires)	.08				
	$W_0 = 18.83$	$W_f = 26.45$				

The results of measurements of simple solutions and of mixtures of solutions are given in Table I. The second column gives, in the case of the original solutions, the mass of anhydrous salt per cubic centimeter. This quantity was obtained by assuming that the salts were pure and that they were represented by the formulas, $CuCl_2 + 2H_2O$, $CuSO_4 + 5H_2O$, $AlCl_3 + 6H_2O$, $Al_2(SO_4)_3 + 18H_2O$, respectively. Solutions No. 2 and No. 13*b* were analyzed by my friend, Mr. L. H. Duschak, Assistant in Chemistry, and the values given are the results of his analysis. In the case of mixtures the composition was determined by using a flask of known volume and weighing the amount of each solution added.

The salts were purchased from Eimer and Amend.

Solutions No. 4, No. 15, No. 16 and No. 17 show considerable difference between the observed and calculated values of K. After No. 4 stood about twenty-four hours a greenish white precipitate formed. This was not noticeable when the observations were made. This precipitate was examined by Mr. Duschak and was found to be a basic chloride of copper. There was a slight trace of aluminium present. It is interesting to note that in the case of solution No. 9 which contained a larger proportion of alu-

TABLE I.

Solution.	Composition.	Density.	Observed. $K.10^6$.	Specific Susceptibility. $K'.10^6$.	Calculated. $K.10^6$.
No. 1.	0.1185 g. $CuCl_2$	1.1012	+0.663	+0.602	
No. 2.	0.0126 g. $MnCl_2$	1.0085	+0.780	+0.773	
No. 3.	0.1732 g. $AlCl_3$	1.1362	−0.862	−0.759	
No. 4.	0.6950 g. No. 1	1.1141	+0.087		+0.418
	0.4191 g. No. 3				−0.318
					+0.100
No. 5.	0.2684 g. No. 3	1.0399	+0.402		−0.204
	0.7715 g. No. 2				+0.596
					+0.392
No. 6.	0.8890 g. No. 2	1.0193	+0.766		+0.687
	0.1302 g. No. 1				+0.078
					+0.765
No. 7.	0.8196 g. No. 2				+0.633
	0.1086 g. No. 1	1.0297	+0.624		+0.065
	0.1015 g. No. 3				−0.077
					+0.621
No. 8.	0.3012 g. No. 2	1.0979	−0.371		+0.233
	0.7967 g. No. 3				−0.604
					−0.371
No. 9.	0.7112 g. No. 3	1.1211	−0.293		−0.540
	0.4099 g. No. 1				+0.247
					−0.293
No. 10.	0.5072 g. No. 1	1.0502	+0.730		+0.305
	0.5431 g. No. 2				+0.420
					+0.725
No. 11.	0.2989 g. No. 1				+0.180
	0.2001 g. No. 2	1.1000	−0.122		+0.155
	0.6010 g. No. 3				−0.456
					−0.121
No. 12.	0.2736 g. $Al_2(SO_4)_3$	1.2297	−0.839	−0.682	
No. 13*b*	0.0174 g. $MnSO_4$	1.0145	+1.016	+1.002	
No. 14.	0.1411 g. $CuSO_4$	1.1336	+0.684	+0.603	
No. 15.	0.2529 g. No. 13*b*	1.1798	−0.396		+0.253
	0.9269 g. No. 12				−0.632
					−0.379
No. 16.	0.7602 g. No. 12	1.1935	−0.280		−0.519
	0.4333 g. No. 14				+0.261
					−0.258
No. 17.	0.5621 g. No. 14	1.0744	+0.837		+0.339
	0.5123 g. No. 13*b*				+0.514
					+0.853
No. 18.	0.3015 g. No. 14				+0.182
	0.1461 g. No. 13*b*	1.1753	−0.199		+0.146
	0.7277 g. No. 12				−0.497
					−0.169

minium chloride solution, no precipitate formed and in this case the observed and calculated values of K agreed very well. The remaining solutions for which there is a considerable difference all contained $Al_2(SO_4)_3$ and in all of them a good deal of aluminium hydroxide was present. It is to be noted that when the relative magnitudes of the quantities added together to give the calculated value of K are taken into account the discrepancies are not so serious as they seem to be. I think the agreement between the observed and calculated values of K for the mixtures is sufficiently good to establish the fact that the magnetic susceptibility is additive for the solutions examined.

I have calculated the specific susceptibility of the salts used and have compared them as far as possible with the values given in Landolt-Börnstein's Tables. The specific susceptibility of a salt was obtained by considering the susceptibility of a solution as the sum of the susceptibilities of the salt and water separately. The method of calculation follows.

Let K_s' = specific susceptibility of anhydrous salt.

K = susceptibility of the solution.

m_s = mass of anhydrous salt per cubic centimeter.

m_w = mass of water per cubic centimeter.

Then $K = m_s K_s' + m_w(-0.8 \times 10^{-6})$.

$$\therefore \quad K_s' = \frac{K + 0.8 \times 10^{-6} m_w}{m_s}.$$

I have also calculated the susceptibility per unit mass of metal in the salt and this quantity I have called K_m'. K_m' is obtained by dividing K_s' by the fraction which expresses the ratio between the mass of metal in the salt and the mass of the salt. I found in the case of $MnCl_2$, $MnSO_4$, $CuCl_2$, and $CuSO_4$ that the susceptibility per unit mass of metal was constant for a given metal. I do not think that this means that the susceptibility of a salt is independent of the acid radical. It seems more probable that the effects upon the susceptibility of the metal, produced by the two acid radicals, are so nearly equal that no difference can be detected by our present methods of measurement. These results agree with those of

Townsend,[1] who found that, for salts of iron, the susceptibility per unit mass of iron was constant for a given state of chemical combination. The metals in the salts I examined were in the same state of chemical combination. The values of K_s' and K_m' are given in Table II. The values of K_m' do not agree in the case of the salts of aluminium. An analysis of the solutions containing these salts may be made later. It is possible the salts were not represented by the formulas, $AlCl_3 + 6H_2O$ and $Al_2(SO_4)_3 + 18H_2O$, respectively.

TABLE II.

Salt.	$K_s' \times 10^6$.	$K_s' \times 10^6$ (Landolt-Börnstein).	$K_m' \times 10^6$.
$CuCl_2$.	12.23	12.3 (L. u. W.) 12.6 L. (J. K.)	25.79
$CuSO_4$.	10.47	10.3 (L. u. W.) 10.4 L. (J. K.) 10.5 (Q.)	26.18
$MnCl_2$.	124.7	117 (J. u. M.) 127 (Q.) 122 (L. u. W.)	285.7
$MnSO_4$.	104.2	98.4 (J. u. M.) 114 (Q.) 100 (L. u. W.)	286.1
$AlCl_3$.	−0.531		−2.62
$Al_2(SO_4)_3$.	−0.189		−1.20

(L. u. W), Liebknecht u. Wills; (J. K.), J. Königsberger; (Q.), Quincke; (J. u. M.), Jaeger u. St. Meyer. L standing after a number means that the susceptibility of air instead of that of a vacuum, is taken to be zero.

G. Meslin[2] found a mixture of water and alcohol that seemed to show a greater specific susceptibility than either liquid separately. This mixture contained 4 parts of water in 100. He found that for absolute alcohol, $K' = 1.03 \times K$ for water, and that for the 4 per cent. mixture $K' = 1.045 \times K$ for water. His method was not capable of detecting this difference with certainty but he found it so many times that he believed there was a real increase in the susceptibility. I thought it would be interesting to repeat this experiment. I measured the susceptibility of absolute alcohol and that of mixtures containing 2 per cent., 4 per cent., 6 per cent. and

[1] Phil. Trans. 1896, p. 545.

[2] Annales de Chimie et de Physique, 1906, p. 188.

8 per cent of water. The alcohol was from E. R. Squibb & Sons and was marked 99.8 per cent. Table III. gives the results of my measurements. In the column headed *calculated* K are given the values of K calculated on the assumption that the susceptibility is additive. The same formula is used as in the case of mixtures of salt solutions. The last column gives the ratio of the specific susceptibility of the mixture to that of water. These values are given to furnish a basis of comparison with Meslin's results. Meslin took the susceptibility of water to be -0.79×10^{-6}.

TABLE III.

	Density (Reduced to T).	T	Observed. $K \times 10^6$	Calculated. $K \times 10^6$	$K' \times 10^6$	$\frac{K'}{K_w}$
Absolute Alcohol (99.8%)	0.7856	24.0°	−0.6536		−0.8320	1.04
2.02% Water	0.7907	24.5	−0.6563	−0.6685	−0.8330	1.0375
4.08% "	0.7942	24.7	−0.6650	−0.6608	−0.8373	1.047
6.21% "	0.8048	20.6	−0.6602	−0.6690	−0.8203	1.025
8.16% "	0.8087	21.0	−0.6731	−0.6718	−0.8323	1.040
Absolute Alcohol (99.8%)	0.7875	21.6	−0.6574		−0.8348	1.044

The water originally in the alcohol is not included in the per cent. of water given in the first column.

It will be seen that K' is greatest for the mixture containing 4 per cent. of water. However the difference between this value of K' and the other values is small and the difference between the observed and calculated values of K is no greater than is to be expected.

In conclusion it appears that the magnetic susceptibility of the liquid mixtures studied is an additive property. The reason for taking solutions of salts of these particular metals was that alloys in varying proportions of aluminium, copper and manganese have been found by Heussler and others to be strongly magnetic, so that the magnetic susceptibility of these alloys is not an additive property.

Throughout the progress of this work I have been indebted to Dr. E. P. Adams for much valuable advice and assistance.

PHYSICAL LABORATORY, PRINCETON.

A NEW TYPE OF ALTERNATING CURRENT GALVANOMETER OF HIGH SENSIBILITY.

By W. S. Franklin and L. A. Freudenberger.

THE alternating current galvanometer to be described is essentially a Kelvin astatic galvanometer modified so as to be suitable for alternating currents.

BB are the two deflecting coils wound in exactly the same manner as the coils of a Kelvin instrument, and having a needle system suspended so as to hang at the centers of the coils.

The needle system differs from the needle system of a Kelvin galvanometer in the fact that the permanent magnets are replaced by unmagnetized soft iron wires inclined 45° to the axis of suspension, *CD*, as shown in Fig. 1. The plane of the magnets lies in the plane of the paper, as shown in the above figure. The two magnets and a light mirror are fastened to a thin glass rod, as shown; and the whole system is suspended at the centers of the coils, *BB*, by a single silk or quartz fiber.

The coils, *AA*, produce a nearly vertical field of about 10 C.G.S. units. This field serves to magnetize the needle system as shown.

The axis of the coils, *AA*, is inclined at an angle of 5° or 10° to the axis of suspension, producing a field in the direction *EF*. This field, *EF*, may be regarded as made up of two components. One, a strong vertical component, *M*, serving to magnetize the needles; the other, a weak horizontal component, *H*, serving to give a directive tendency to the needle system.

In Fig. 1, the arrows, *M* and *H*, indicate the directions of the fields produced by one half cycle of current, (that is, *M* and *H* are the components of the field *EF*). The needle system is then magnetized as shown. If, at this instant, the current to be measured is sent through the coils, *BB*, a torque acts on the needle system tending to turn the magnets to a position at right angles to the plane of the paper. The current for the coils, *BB*, is, of course, obtained from the same source as the current for the coils, *AA*.

During the succeeding half cycle of alternating current, the field, *EF*, is reversed (thus reversing *M* and *H* and the polarity of the needle system); while the current in the coils, *BB*, reverses simultaneously, thus giving a torque in the same direction as before.

It is not necessary that the two currents, — in the coils, *AA* and *BB*, — be strictly in phase with each other. Where the two currents differ in phase, the tangent of the angle of deflection is proportional to the cosine of the angle of phase difference.

It is evident that the galvanometer will indicate equally as well when the coils, *AA* and *BB*, are supplied by direct current, instead of alternating current.

Adjustments.

1. The coils, *AA*, rest on leveling screws fastened to the base of the instrument, so that the axis of *each* coil can be placed in any position (not differing greatly from the vertical direction). Thus the angle, *COE* (in the plane of the paper), may be varied, thus adjusting the strength of the horizontal component, *H*, and consequently adjusting the strength of the directive tendency of the needle system. The angle, *COE*, can not be made too small (small value of *H*), as the directive tendency becomes so small that the "zero" position is unstable. Throughout this adjustment the two coils, *AA*, are kept parallel to each other.

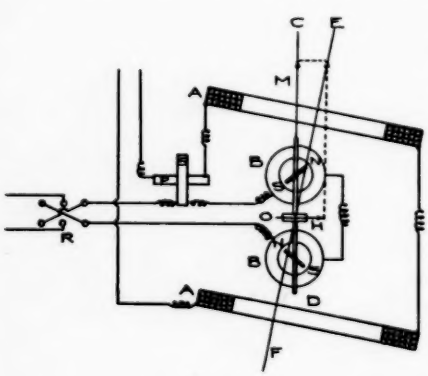

Fig. 1.

2. To adjust the "zero" position of the suspended system, that is to place the magnets in the plane of the paper (Fig. 1), the angle, *COE* (in a plane at right angles to the plane of the paper), is varied — for one coil only, of the two coils, *AA*.

The two adjustments outlined above correspond to the adjustments of the "zero" of an ordinary Kelvin instrument by means of a "controlling" magnet.

3. The field produced by the coils, *AA*, induces small E.M.F.'s in the coils, *BB*. Further the E.M.F.'s induced in the coils, *BB*, are opposite in sign, since the coils, *BB*, are connected in opposition. When the galvanometer is short-circuited at the reversing switch, "*R*," there will usually be sufficient E.M.F. induced in the coils, *BB*, to cause a deflection of a few centimeters (scale divisions). It is possible to place the two coils, *AA*, symmetrically with respect to the field, *EF*, so that no deflection is produced on short circuit, and at the same time satisfy adjustments 1 and 2 above. This adjustment, however, is very tedious and can be eliminated by using a small transformer without iron, with a movable secondary. The primary of the transformer is connected in series with the coils, *AA*, and the movable secondary in series with the coils, *BB*, as shown in Fig. 1. It thus becomes possible to make each of the three adjustments independently of each other.

Three instruments of different resistances, have thus far been built by the writers. The first two instruments built, are not as sensitive, however, as they might be. The design of a sensitive instrument is exactly the same as the design of a Kelvin galvanometer, *i. e.*, the coils (*BB*) must be wound to the theoretical shape,[1] and the best size of wire chosen. This size of wire lies in the vicinity of No. 36 *B* and *S* gauge, single silk covered.

In two of the instruments constructed, the sensibility of the coils (*BB*) was also tried as an ordinary Kelvin astatic galvanometer by replacing the soft iron magnets with a permanent magnet suspension. From the results of these tests, the sensibility of the alternating current instrument varies from one third to one sixth of the sensibility of the same instrument as an ordinary Kelvin galvanometer.

No serious difficulty was experienced from any disturbing effect of the earth's field. The earth's field might be eliminated by surrounding the entire galvanometer by a massive iron cylinder — with perhaps a slight increase in sensibility.

The following are the results of the sensibility tests of the alternating current instruments.[2]

[1] See Gray's Absolute Measurements.

[2] The sensibility of the best types of telephone receivers is about 10^{-6} amperes. Resistance 75 ohms.

Instrument No. 1.

Coils (*BB*) $1\frac{3}{4}''$ in diameter.

Needle chamber $\frac{5}{16}''$ in diameter.

Magnets $\frac{1}{4}''$ long.

Wound with No. 36 *B* and *S* gauge, double silk covered wire.

Resistance, 2,306 ohms.

Sensibility $= 4 \times 10^{-9}$ amperes per mm., with scale at one meter's distance.

Instrument No. 2.

Coils $1\frac{1}{4}''$ in diameter.

Needle chamber $\frac{1}{32}\frac{7}{2}''$ in diameter.

Magnets $\frac{1}{2}''$ long.

Wound with No. 20 *B* and *S* gauge, single cotton covered wire.

Resistance, 1.75 ohms.

Sensibility $= 6 \times 10^{-7}$ amperes per mm. per meter.

Instrument No. 3.

Coils $\frac{5}{8}''$ in diameter.

Needle chamber $\frac{3}{16}''$ in diameter.

Magnets made of a single 10 mil iron wire, $\frac{1}{8}$ long.

Wound with No. 33 *B* and *S* gauge, single silk covered wire.

Resistance, 21 ohms.

Sensibility, 6×10^{-8} amperes per mm. per meter.

The sensibilities of the above instruments as ordinary Kelvin galvanometers, are

No. 1. 1.4×10^{-9} amperes per mm. per meter.

No. 2.

No. 3. 1.0×10^{-8} amperes per mm. per meter.

A Kelvin galvanometer has since been built by Mr. McFarlin, a student at Delaware College, with a sensibility of 1.0×10^{-9} amperes per mm. per meter; coils 1'' in diameter, needle chamber $\frac{3}{16}''$ in diameter. Magnets $\frac{1}{8}''$ long. Wound with No. 36 *B* and *S* gauge, single silk covered wire. Resistance, 100 ohms. This instrument has the same sensibility as No. 1, with only 100 ohms resistance, as against 2,306 ohms for No. 1. The coils of No. 1 departed rather widely from the theoretical shape.

A slight gain in sensibility may, of course, be obtained by properly grading the wire of the coils; but the gain hardly warrants the difficulties of winding.

The above alternating current galvanometer was developed to meet the demand for a sensitive alternating current instrument required for a new method for measuring electrolytic resistances — the subject of a grant made by the Carnegie Institution of Washington.

South Bethlehem, Pa.,
July, 11, 1906.

THE VAPOR PRESSURE OF CARBONIC ACID AT LOW TEMPERATURES.

BY JOHN ZELENY AND ROY H. SMITH.

1. Carbonic acid is remarkable for having a relatively high vapor pressure when in the solid state. At its melting point this pressure is greater than five atmospheres. The boiling or sublimation point, where the vapor pressure is equal to that of one atmosphere, is therefore considerably (over 20° C.) lower than the melting point.

The vapor pressures of carbonic acid, between 0° C. and the boiling point, have been measured by several observers but the results are not in good agreement.[1] For temperatures below the boiling point, we know of but one set of observations.[2]

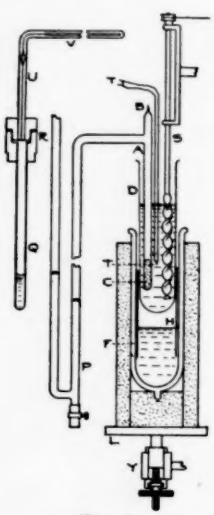

Fig. 1.

The determinations described in this paper extend over the range from $-7°$ C. to the lowest temperature at which the pressure is appreciable.

2. The apparatus used for making the measurements is represented diagrammatically in Fig. 1.

The solid carbonic acid, *C*, was contained in the glass tube, *A*, whose lower end was immersed in pentane in the glass tube, *D*. The temperatures were measured by the thermo-electric couple, *T*, one of whose junctions was placed near to the carbonic acid tube while the other was kept in ice.

The pentane was agitated vigorously by means of the stirrer, *S*, which was operated by a water motor, and under these conditions

[1] See M. Faraday, Phil. Trans., 1845, p. 155. Kuenen and Robson, Phil. Mag. (6), 3, p. 149.

[2] Du Bois and Wills, Beibl. zu den Ann. der Physik, 24, p. 428.

it was found that the junction indicated the same temperature in all parts of the bath.

The pentane bath was brought to any desired temperature by means of the liquid air contained in the Dewar vessel, *F*. The stand, *L*, which carried this vessel was arranged so that it could be moved vertically by the slow-motion screw, *Y*. By watching the temperature as indicated by the deflection of a galvanometer and carefully moving this screw, the temperature of the pentane could be maintained at a constant value to 0°.1 C. for considerable periods of time, which enabled all of the contents to assume a common temperature before a reading was taken. A metal cylinder, *H*, was fastened to the lower end of the tube, *D*, and dipped into the liquid air. This was a great aid in maintaining some of the temperatures as it made the changes produced by moving the liquid air vessel more gradual and uniform.

Two different arrangements of the apparatus were used, one for the low pressures and one for the high pressures.

3. For the low pressures, the tube, *A*, having a diameter of 1 cm., was connected by a glass tube to the open mercury manometer, *P*. Pressures up to three atmospheres could be measured by this manometer, the readings being taken with the aid of a simple cathetometer together with the reading of the barometer.

The apparatus was filled with pure carbonic acid in the following manner. A small glass tube was introduced into the tube, *A*, through the open end, *B*, and fastened to it by rubber tubing. Carbonic acid from a cylinder of commercial liquid carbonic acid was allowed to flow into *A* through this tube, and passed out through the gauge, *P*, from which nearly all of the mercury had been removed previously. After the air had been displaced the lower end of the tube, *A*, was introduced into a flask of liquid air. The carbonic acid coming from the jet froze at the bottom of the tube while the air mixed with it passed out. The tube, *A*, was lowered little by little until it was filled with solid carbonic acid for about two thirds of its total length. The tube was then partly raised from the liquid air and after the temperature had risen so that the pressure inside was greater than an atmosphere, the end, *B*, was hermetically sealed with a blow-pipe, the auxiliary glass tube having been withdrawn previously.

The solid carbonic acid was then allowed to vaporize from the top and to pass out through the gauge until a length of about 3 cm. only was left. The gas coming out of the open gauge was tested several times and found to contain only about one fortieth of 1 per cent. of impurities, although the original carbonic acid had 1.7 per cent. The tube, *A*, was now introduced into the cooled pentane bath and the taking of observations begun.

4. The tube, *Q*, was used for the higher pressures. This was 25 cm. long and had an outside diameter of 6 mm. and an inside one of 4.5 mm. It was joined to the closed air gauge, *V*, by means of the brass coupling, *R*, into which the two parts were sealed with cement. Apparatus made entirely of glass, with the gauge sealed in as a side joint, was first tried but in all except one case the whole exploded with considerable violence after the pressure had increased to about 60 atmospheres.

The tube, *Q*, was nearly filled with solid carbonic acid in the manner described in the previous section. The gauge, *V*, was then partly screwed on and its mercury thread was forced down to the open end of its tube. The vaporized carbonic acid escaped through the loose joint of the brass coupling and the apparatus was thus cleared of air. When all but a small portion of the solid carbonic acid had disappeared, the coupling was screwed tight against a leather washer by two powerful wrenches. The joint thus made was practically perfect as no leakage was ever detected after standing several days. The amount of carbonic acid left in the tube was such that liquid began to form in the tube when it was cooled a few degrees below 0° C.

The gauge, *V*, was filled with dry air, having a length of 69 cm. at atmospheric pressure. The tube was 1.2 mm. in diameter and was carefully calibrated. The liquid carbonic acid underwent so much supercooling that it usually froze so explosively as to shatter the mercury thread in the gauge. This difficulty was overcome by having a 15 cm. length of thermometer tubing, *U*, with an enlargement blown at its center, placed between the gauge proper and the brass coupling.

The readings of the gauge were corrected for inequality of the bore, for temperature, and for deviations from Boyle's law. The

last corrections were obtained by interpolation from Amagat's values.[1]

5. The thermo-electric couple used for measuring the temperatures was made of nickel and iron. These metals were chosen because their thermo-electric power changes less with temperature than for most metals so that the calibration of the couple does not necessitate the use of so many temperatures. The readings were taken with a d'Arsonval galvanometer, the deflections being brought to zero aperiodically after each reading so as to obtain the correct zero point.

The couple was calibrated by determining the deflections for six known temperatures.

The temperatures used, besides that of 0° C., were obtained as follows:

(*a*) A pentane bath, stirred vigorously, was maintained at a constant temperature whose value was read by a calibrated thermometer as — 29°.2 C.

(*b*) The temperature of a thick mixture of carbonic acid snow and ether was taken as — 78°.77 C.[2] for the barometric pressure 73.5 cm.

(*c*) The boiling point of ethylene, for the barometric pressure 74.0 cm. was taken as — 103°.9 C.[3]

(*d*) The freezing point of ethylene was used as — 169° C.[4]

(*e*) The temperature of liquid air was determined from its density.[5] This was conveniently measured with sufficient accuracy by weighing a small mouthed, 600 c.c. Dewar flask filled with the liquid up to a fixed point for which the volume had been determined and reduced to the temperature of liquid air.

The galvanometer deflections obtained with the above temperatures were plotted on a large scale and the curve, drawn through the points, was then used for getting the temperature corresponding to any deflection.

The galvanometer had a large resistance of manganin wire in

[1] Compt. Rend., 1884, p. 1153.

[2] J. Zeleny and A. Zeleny, this volume.

[3] Travers, Study of Gases, p. 243. (Wroblewski, Witkowski, Ramsey and Travers.)

[4] K. Olzewski, Wied. Annalen (37), p. 337.

[5] Behn and Kiebitz, Annal. der Physik. (4), 12, p. 425.

series with it, in order to diminish the errors, due to changes of the room temperature, to a negligible quantity.

6. The final observations were made on several days and over a hundred readings were taken. The corrected results were then plotted all together on a large scale and those for the lower pressures were also plotted separately on a still larger scale. The results agreed well among themselves not only with either form of apparatus but also where the readings for the two forms overlapped.

The curves drawn through the plotted points were then used to find the vapor pressure corresponding to any temperature.

The results obtained in this way are given in columns II. and III. of the following tables.

TABLE I.

Vapor Pressures of Liquid Carbonic Acid.

Temperature. °C.	Vapor Pressure in Atmospheres.	Vapor Pressure in Meters of Mercury.	K. and R. Meters of Mercury.
− 7	27.80	21.13	
−10	25.83	19.63	19.8
−12	24.50	18.62	
−15	22.46	17.07	17.0
−18	20.65	15.69	
−20	19.52	14.83	14.7
−22	18.33	13.93	
−25	16.74	12.72	12.5
−28	15.10	11.48	
−30	14.21	10.80	10.6
−32	13.30	10.11	
−35	11.92	9.06	8.97
−38	10.67	8.11	
−40	9.88	7.51	7.46
−42	9.18	6.98	
−44	8.53	6.48	
−46	7.89	6.00	
−48	7.30	5.55	
−50	6.73	5.115	5.02
−52	6.18	4.70	
−54	5.66	4.31	
−56	5.19	3.945	
−56.4	5.11	3.911 Triple Point.	
−58	4.75	3.610 Supercooled.	
−60	4.35	3.306 "	3.27
−62	3.96	3.01 "	
−64	3.58	2.721 "	
−65.5	3.30	2.508 "	

TABLE II.

Vapor Pressures of Solid Carbonic Acid.

Temperature. ° C.	Vapor Pressure in Atmospheres.	Vapor Pressure in Centimeters of Mercury.	K. and R.	
− 56.4	5.11	391		
− 57	4.85	368.5		
− 58	4.51	343		
− 59	4.20	319		
− 60	3.92	298	302	
− 61	3.67	279		
− 62	3.43	260.5		
− 63	3.20	243		
− 64	2.98	226.5		
− 65	2.78	210	211	
− 66	2.59	195.5		
− 68	2.21	168		
− 70	1.88	144	143	
− 72	1.638	124.0		
− 74	1.395	106.0		
− 75	1.283	97.5	97	
			D. and W.	Z. and Z.
− 77	1.102	83.9	88.5	84.0
− 78.2	1.00	76		
− 80		65.7		66.6
− 82		55.8		57.0
− 84		47.3		48.4
− 85		43.5	51.0	44.6
− 86		40.0		41.2
− 88		34.0		35.0
− 90		28.8		29.2
− 92		24.1		24.4
− 94		20.2		20.4
− 96		17.0		16.8
− 98		14.1		13.9
−100		11.9		11.3
−102		9.9	11.0	9.2
−104		8.0		7.4
−106		6.4		6.0
−108		5.3		4.9
−110		4.3		4.0
−112		3.4	4.0	3.25
−114		2.7		2.7
−116		2.2		
−118		1.8		
−120		1.4		
−122		1.1		
−124		.8	.5	
−126		.6		
−128		.45		
−130		.25		
−132		.15		
−134		.1		

The values in the column marked *K.* and *R.* are those given by Kuenen and Robson.[1] Considering the different methods used in making the determinations the results are seen to be in fair agreement with the corresponding ones here obtained. The values under *D.* and *W.* are those obtained by du Bois and Wills[2] for the temperature of carbonic acid snow at different pressures. Their values are in general higher than those obtained by us. The value of the boiling point given by them is $-79°.2$ C., which is 1° lower than that given in our tables. By raising all of their temperatures 1°, the two sets of results are brought into much better agreement.

In the last column of Table II., under *Z.* and *Z.*, are added the values recently obtained in this laboratory[3] for the temperatures of carbonic acid snow and its mixtures with ether and alcohol when these are maintained under different pressures. They differ but little from these determinations.

7. It was noticed that the amount of impurity in the low pressure apparatus increased somewhat during a set of observations. This was inferred from the value of the pressure for the temperature of liquid air, which at the start was practically zero, but which towards the end of a set of observations had increased to more than 0.1 cm. The supposed reason for this is that the solid carbonic acid contained a trace of absorbed air. When the pressure of the vapor was increased to two or three atmospheres some of the solid vaporized, freeing the absorbed air. On recooling the tube, the carbonic acid was condensed, but the air was nearly all left free in the tube. By repeated heating and cooling of the tube the amount of impurity was increased in this way. The value of the pressure for the temperature of liquid air was reduced to zero again by allowing the accumulated gas to bubble out through the manometer. In any case the value of the pressure obtained for the temperature of liquid air was subtracted from the other readings taken.

The triple point was determined in the following way. The frozen carbonic acid in the high pressure apparatus was warmed slowly and the pressure noted as it gradually increased. When

[1] Loc. cit.
[2] Loc. cit.
[3] J. Zeleny and A. Zeleny, loc. cit

the carbonic acid began to melt the pressure became constant and remained so for some time, so that its value could be determined with precision. It was found to be 5.11 atmospheres. The temperature of the triple point was determined from the temperature-pressure curve for the liquid carbonic acid, by finding the temperature corresponding to this pressure of 5.11 atmospheres. The value was found to be $-56°.4$ C.

The corresponding values obtained by Kuenen and Robson are 5.10 atmospheres and $-56°.2$ C. and those obtained by Villard and Jarry[1] are 5.1 atmospheres and $-56°.7$ C.

By means of the formula for the latent heat of evaporation,

$$L = (v_v - v_l) T \frac{dp}{dT},$$

Kuenen and Robson[2] calculated the value of the latent heat at the boiling point to be 121 calories, by taking 355 as the specific volume of the vapor of carbonic acid at the boiling point and using for dp/dT, 5.5 cm. per 1° C., the value obtained by du Bois and Wills.[3] This result is much smaller than the experimental values obtained by Behn[4] (142.4 calories) and by Favre and Silbermann[5] (142.2 calories). The value of dp/dT obtained from our curves is 6.35 cm. per 1° C., and using this number the value of L becomes 140 calories. which is in very good agreement with the experimental results.

PHYSICAL LABORATORY,
UNIVERSITY OF MINNESOTA,
June 29, 1906.

[1] Compt. Rend., 120, p. 1413.
[2] Phil. Mag. (6), 3, p. 627.
[3] Loc. cit.
[4] Annal. der Physik, 1, p. 272.
[5] Ann. de Chim. et de Phys. (3), 37, p. 470.

THE SPARK DISCHARGE IN GASES AND VAPORS.

BY JOHN E. ALMY.

PASCHEN'S law,[1] giving the relation between gas pressure and spark length, is an important advance in the generalization of the phenomena of spark discharge in gases. Carr's[2] verification of the law shows it to hold for a wide range of pressure. Peace[3] first noted the existence of a "minimum" spark potential, and Carr, (loc. cit.), has shown that, — at least for rather low pressures, — there are critical points of spark length and pressure such that if the spark gap is diminished below the critical distance, with pressure constant, or, if the pressure is reduced below the critical value, with constant spark gap, — the spark potential, *increases* with *decreasing* spark length, or *decreasing* pressure as the case may be. The work of Earhart,[4] Kinsley,[5] and Hobbs,[6] seems to have thrown some doubt upon the entire generality of the phenomenon of increasing spark potential with decreasing spark length, however there is evidence suggesting that the phenomena studied by these observers were of the nature of coherer discharge rather than spark discharge.

De la Rue and Müller[7] concluded that the spark discharge passes more readily between electrodes of aluminium than between any other metals; Righi, Peace, and Carr were unable to detect any difference in spark potentials depending upon electrode material. The writer[8] of this paper has pointed out the probability that any such difference due to electrode material would be of the same order as the differences in the "cathode fall" when the same metals are used in the Crookes tube, and consequently would be small

[1] Paschen, Wied. Ann., 37, p. 79, 1889.
[2] Carr, Proc. Roy. Soc., 71, p. 374, 1903.
[3] Peace, Proc. Roy. Soc., 52, p. 99, 1892.
[4] Earhart, Phil. Mag., (6), 1, p. 147, 1901.
[5] Kinsley, Phil. Mag., (6), 9, p. 692, 1905.
[6] Hobbs, Phil. Mag., (6), 10, p. 617, 1905.
[7] De la Rue and Müller, Phil. Trans., 169, pt. 1, p. 93, 1898.
[8] Almy, Phys. Rev., 20, p. 382, 1905.

beyond the possibility of detection, in most gases. In the case of hydrogen it was found that there is a clearly determined difference in the spark potentials for a given spark length, when different metals are used as electrodes.

Roentgen[1] concluded that the minimum potential which will maintain a discharge between a point and a plane, as electrodes, for different gases with same distance between electrodes and same gas pressure, varied inversely as the mean free path of the gas molecules. The insufficiency of the data of spark potentials in various gases and vapors and the fact of the errors due to "lag" of the spark, and differing electrodes, seem to warrant new determinations of spark potentials in various gases and vapors to test with greater care the correctness of Roentgen's hypothesis as applied to the spark discharge. Such was the purpose of the work to be described, the gases and vapors being those which gave as wide a range of mean free molecular path as could be readily obtained.

It has been the usual assumption that spark potentials at a given pressure are a linear function of the spark lengths; this is by no means exactly true; at atmospheric pressure, for any considerable range of spark length it is not even approximately so. Consideration of the data given by Paschen, and by Orgler,[2] shows, however, that the quantity—

$$\frac{1}{P}\cdot\frac{dV}{dx},$$

is a function of the spark potential, alone, being very approximately constant for all pressures and spark lengths, so long as the potential range used is the same.

Consequently this quantity,

$$\frac{1}{P}\frac{dV}{dx} = K,$$

may be taken as characteristic of a given gas or vapor, independent of gas pressure, spark length, or electrode material, if the range of potential used in its determination is the same in all cases. Hence, spark potentials, in various gases and vapors, at various pressures, were determined with potentials varying from 360 to 900 volts, and the values of the gas constant, K, calculated.

[1] Roentgen, Gottingen Nachr., p. 390, 1878.

[2] Orgler, Ann. der Phys., 1, p. 169, 1900.

The apparatus used and the method were the usual ones; a discharge tube with two spherical electrodes having curvature of 10 cm. radius, was connected with a system of wash flasks and drying tubes for obtaining the pure, dry gas or vapor desired, and to an air-pump to facilitate the filling of the tube. The upper electrode was carried on a screw allowing measurement of the spark gap, to .003 mm. without any rotation of the electrodes. A quartz window, *Q*, Fig. 1, served for the illumination of the light from an electric arc, which is effective in eliminating the "lag" of the spark. A battery of storage cells gave potentials up to 1,000 volts, a Weston voltmeter was used to measure the spark potentials. This voltmeter was calibrated by comparison with a high-accuracy standard Weston voltmeter.

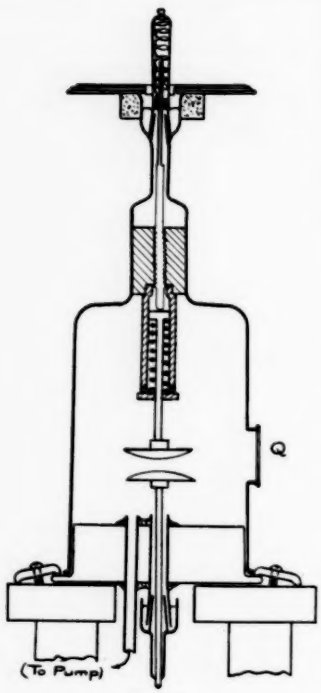

Fig. 1.

A rheostat, consisting of two tubes, one of distilled water, the other of amyl alcohol with a small amount of cadmium iodide in solution, in series with the battery with the voltmeter and spark gap in parallel were shunted off the rheostat, enables one to vary the potential applied to the spark electrodes, at will. The tube of water is of advantage in obtaining almost the whole potential of the battery without the danger of short-circuiting the battery when very short sparks are used.

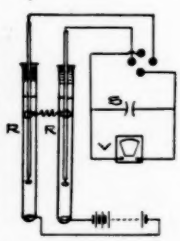

Fig. 2.

The electrical connections are shown, diagrammatically in Fig. 2, *S*, being the spark gap, *V*, the voltmeter, and, *R*, *R*, the rheostat tubes. In taking the observations the spark gap is first closed completely, a small potential (30 to 50 volts), being used to test the short circuit, then the spark electrodes are moved apart, by very

minute steps, the potential being applied after each step to detect the point where the electrodes first separate care being taken that the potential was not applied to the spark gap when the electrodes were being moved apart. Having thus obtained the zero point of the spark gap, the electrodes were then separated the desired distance and the potential then gradually increased until a spark discharge occurred, the passage of a spark being evident from the sudden drop in the reading of the voltmeter.

The considerable variation shown by the comparison of the best previous determinations of spark potentials made it advisable to repeat the determinations for some of the permanent gases, so that results obtained under like conditions may be used in comparing the different gases and vapors.

Air which was thoroughly dried from standing in the apparatus with phosphorous pentoxide 48 hours or more, gave the following results:

Air.

Pressure 73.8 cm.			Pressure 30 cm.			Pressure 6 cm.		
x (cm.).	V (volts).	K	x (cm.).	V (volts).	K	x (cm.).	V (volts).	K
.001	345	1285	.002	322	1033	.01	340	1113
.002	440	1209	.004	384	1067	.02	407	1113
.003	526	1070	.006	448	1033	.03	474	1100
.004	605	954	.008	510	1113	.04	540	1013
.005	677	1030	.010	578	913	.05	601	987
.006	743		.012	633	913	.06	660	1000
			.014	685		.07	720	
Mean values of K,		1090			1016			1043

Hydrogen,—generated from zinc with pure, hydrochloric acid, was purified by passing successively through solutions of potassium per-

Hydrogen.

Pressure 73.5 cm.			Pressure 30 cm.			Pressure 6 cm.		
x (cm.).	V (volts).	K	x (cm.).	V (volts).	K	x (cm.).	V (volts).	K
.001	245	700	.004	300	666	.02	345	700
.002	296	680	.006	340	666	.03	387	813
.003	346	667	.008	380	700	.04	425	750
.004	395	670	.010	422	633	.05	480	600
.006	500	662	.012	460	713	.06	516	543
.008	604		.014	503	700	.08	560	
			.016	545				
Mean values of K,		676			680			676

manganate, potassium hydrate, and alkaline pyrogallic acid and dried in tubes of solid KOH and phosphorous pentoxide, giving the following results:

Carbon Di-sulphide Vapor. — Ordinarily pure carbon di-sulphid is by no means a simple substance, but contains various decomposition products. The CS_2 used was some especially cleaned and dried for electro-optical purposes and was almost wholly free from obnoxious odors, a clear, almost colorless, liquid. The vapor of this liquid gave the following results:

Carbon Di-sulphide.

Pressure 30 cm.			Pressure 28.5 cm.			Pressure 16 cm.		
x (cm.).	V (volts).	K	x (cm.).	V (volts).	K	x (cm.).	V (volts).	K
.00166	313	4480	.00166	384	3880	.00166	304	4950
.0025	425	3400	.0025	475	3650	.0025	370	4875
.0033	510	3400	.0033	560	2800	.0033	435	3975
.00417	595	3320	.00417	627	2900	.0050	541	2850
.0050	678		.0050	694		.0067	617	2850
						.0083	694	2780
						.010	769	
Mean values of K,		3650			3320			3 710

Chloroform. — Chemically pure chloroform, dried with fused $CaCl_2$ gave the following results:

Chloroform.

Pressure 13.5 cm.		
x (cm.).	V (volts).	K
.005	510	2370
.010	670	2520
.015	840	2615
.020	1017	
	Mean value of K,	2500

(The data given here are in each case the average of several distinct determinations, the pressure being the same in all.)

Benzol. — In working with benzol, (benzene), it was noticed that the spark potential for a given spark gap, and also the color of the discharge glow, obtained from the first one or two discharges after the discharge tube is filled with fresh vapor is essentially different

from that of succeeding sparks. This is probably due to the decomposition of the vapor by the discharge and a consequent change of the ions which carry the discharge, the first spark produces a brilliant green light while later ones give the pinkish tinted glow, the discharge being probably carried by CH_2 or CH_3 ions. A rapid deposition of carbon upon the electrodes as sparks pass seems to confirm the supposition of the decomposition of the benzol.

In the results given below, Set I. are observations taken in each instance, the first spark after the electrode had been freshly polished and the vapor fresh; Set II. are data obtained by taking mean values of the first three sparks in each instance; and Set III. are the results obtained after a number of sparks had passed in each instance; Set I. representing then, the results obtained with the benzol vapor unmixed with impurities while the other sets show the results of increasing amount of impurities introduced.

Benzol.

Set I. Pressure 5 cm.			Set II. Pressure 7 cm.			Set III. Pressure 7.7 cm.		
x (cm.).	V(volts).	K	x (cm.).	V(volts).	K	x (cm.).	V(volts).	K
.010	565	4450	.010	601	3230	.005	520	2600
.015	675	4040	.015	715	3450	.010	620	2210
.020	778	4280	.020	835	3000	.015	705	2210
.025	885		.025	935		.020	790	2340
						.025	880	
Mean values of K,		4240			3230			2340

Ammonia. — Commercial ammonia, taken from a cylinder of the gas was used, being dried by passing through tubes containing solid KOH in small fragments. It is a well known fact that ammonia is decomposed under the action of the electric spark, giving free nitrogen and hydrogen; this was very evident from the observations, the spark potentials dropping rapidly with use of the gas to the values usually obtained for nitrogen, and with extended use falling nearly to the values obtained in hydrogen. A complete set of "first spark" reading was not obtained, the first two readings in each set may be taken as indicative of the results which would be obtained if no decomposition occurred.

Ammonia.

Pressure 32 cm.			Pressure 20 cm.			Pressure 10 cm.		
x (cm.).	V (volts).	K	x (cm.).	V (volts).	K	x (cm.).	V (volts).	K
.002	485	1406	.002	430	1416	.005	400	1400
.005	620	875	.005	515	810	.010	470	900
.010	760	750	.010	596	810	.015	515	800
.015	880		.015	677	1010	.020	555	
			.020	778	1010			
			.025	890				

Mean value of K from first two sparks, 1407.
Mean value of K from all the other observations, 882.

Ether. — The best grade of commercial ether obtainable, dried with calcium chloride, gave the following data:

Ether.

Pressure 20 cm.		
x (cm.).	V (volts).	K
.003	520	3300
.005	620	2500
.010	870	2500
.012	970	
		Mean value of K, 2767

Nitrogen. — From recent, evidently very careful, determinations of spark potentials in nitrogen by Hurst,[1] the values of the gas constant, K are calculated for nitrogen. The results represent averages for various pressures as Hurst gives his spark potentials as function of the product, Px (pressure times spark length).

Nitrogen.

$P.x$ (cm.²).	V (volts).	$\frac{dV}{d(Px)} = K$.
.134	340	1110
.170	380	1140
.240	460	1000
.284	505	730
.420	650	

[1] Hurst, Phil. Mag. (6), 11, p. 535, 1906.

In comparing the gas constants obtained in the work described above, with the mean free paths of the molecules of the different gases and vapors used it is necessary to deduce the free paths for the particular temperature at which the gas stood during the experiment. According to Meyer (cf. Kinetic Theory of Gases), the viscosity of a gas or vapor depends upon the temperature in the following manner:

$$\eta_t = \eta_0(1 + Bt)^{\frac{1}{2}},$$

where B is the coefficient of cubical expansion of the gas, η, the coefficient of viscosity, and t, the temperature, centigrade.

But we have

$$\eta_0 = .309\ \delta_0 \bar{v}_0 \lambda_0$$

and

$$\eta_t = .309\ \delta_0 \bar{v}_t \lambda_t$$

in which δ, $\bar{v}$, and λ refer to density of the gas, mean square speed, and mean free path of the gas molecules, respectively, and

$$\frac{\bar{v}_0}{\bar{v}_t} = \frac{1}{(1 + Bt)^{\frac{1}{2}}}, \text{ hence } \lambda_t = \lambda_0(1 + Bt).$$

The values of mean free path for the different gases and vapors, taken from Landolt and Bornstein's *Tabellen*, at the temperatures at which the substances were used, together with the gas spark-constants determined for spark potentials between 400 and 900 volts are given in the following table. As the values of mean free paths given by different authorities differ considerably in some instances the values given by the most recent determinations are used.

Substance.	Spark Constant K, (volts/cm.^{2})	Mean Free Path, $\lambda \cdot 10^8$ (cm.).	Product $K \cdot \lambda \cdot 10^{-8}$
Hydrogen	675	1630	1.10
Carbon di-oxide	906	680	.61
Nitrogen	995	990	.985
Air	1050	1025	1.07
Ammonia { first spark	1407	740	1.04
Ammonia { averages	880	740	.65
Carbon di-sulphide	3560	311	1.10
Carbon di-sulphide	3560	274	.975
Chloroform	2500	256	.64
Ether	2767	215	.59
Benzol { first spark	4240	235	1.01
Benzol { later ones	2340	235	.55

It is evident that in the greater number of cases, the product, $K\cdot\lambda$, is approximately constant, or that the function, K, which represents the gas-characteristic in the determination of sparking potentials, is inversely proportional to the mean free path of the gas molecule. The deviations from this law, shown by some of the vapors tested may in all probability be rightly attributed to the decomposition of the gas or vapor so that the medium through which the discharge takes place is not the substance which originally filled the discharge tube. The fact that carbon di-sulphide, of which the decomposition products are solids and hence precipitate out when formed, is the only compound substance which does not show marked difference between first sparks and succeeding ones, obeys the law together with the elemental substances, seems confirmatory to this hypothesis. Again the case of carbon di-oxide is suggestive; it is a well known fact that this gas is dissociated in the electric discharge. Geissler tubes filled with CO_2 under the action of the discharge come ultimately to show almost wholly the spectral lines of the mon-oxide, CO. Now the observations of Orgler and Paschen with carbon di-oxide are such as give a mean value of the constant, K, of 906, (which is obviously smaller than would have been obtained using lower spark potentials), and this quantity, multiplied by the mean free path of the carbon mon-oxide molecule, which is $1040\cdot 10^{-8}$, gives for the value of the product, $K\lambda$, the number, $.94\cdot 10^{-2}$ which is approximately the same as that for the permanent gases.

To sum up:

It seems that the assumption of Roentgen is supported by the results of experiment, namely, that the spark potentials in a gas or vapor is a function of the mean free path of the molecule of the gas or vapor, and in fact an inverse function; that is — for a given spark potential, the quantity,

$$\frac{1}{P}\frac{dV}{dx} = K = f\left(\frac{k}{\lambda}\right)$$

the quantity, k, being in turn a function of the spark potential, V, but for a limited range it is approximately constant. And, to the same degree of approximation to which Paschen's law holds, the

potential, V, necessary to produce a spark discharge through a distance, x, in any gas is expressed by the equation,

$$V = V_0 + P\left\{f\left(\frac{k}{\lambda}\right).(x - x_0)\right\},$$

in which

V_0 = the minimum spark potential for the gas and electrodes used,

x_0 = the distance of the minimum potential spark at the pressure used,

λ = the mean free path of the molecules of the gas used,

k = a gas spark constant, which has the same value for all gases and vapors, (so long as the spark is not effected by decomposition products of the discharge), but varying with the discharge potential concerned.

THE BRACE LABORATORY OF PHYSICS,
LINCOLN, NEBRASKA, July, 1906.

THE CAPACITY AND RESISTANCE OF ALUMINIUM ANODE FILMS.[1]

BY C. McCHEYNE GORDON.

THERE is formed on aluminium when used as an anode in most solutions, a film which is highly insulating in character so long as the voltage applied is not too high, or the direction of the current is not reversed. These films have been the subject of a large number of investigations; interest in them having been especially lively during recent years since the possibility of taking advantage of the asymmetric resistance for rectifying alternating currents has been realized. These investigations have proven that the resistance of the films and the voltage at which the resistance begins to decrease rapidly, generally called the critical voltage, vary with the electrolyte used as well as with the temperature. They have shown however considerable conflict of evidence and opinion as to the chemical constitution and reasons for the asymmetry of resistance and its breaking down at higher voltages.

No extensive study of the electric capacity of these films has heretofore been made. Scott[2] made a few measurements on the polarization capacity of aluminium in connection with a number of other metals, while the electrodes were subjected to a definite polarization, but his measurements on aluminium are all taken at low voltages — not greater than 1.75 volts; and only in one solution — sulphuric acid. A number of others have given capacity values, but without explicit statements as to conditions or method of measurement.

METHOD OF MEASUREMENT.

The method used to measure the capacity is that developed by the writer[3] at the suggestion of Nernst for the measurement of the

[1] A summary of this paper was given at the Ithaca meeting of the A.A.A.S., July, 1906.

[2] Scott, Wied. Ann., 67, p. 388, 1889.

[3] Gordon, Wied. Ann., 61, p. 1, 1897.

capacity of polarization. It is the well known wheatstone bridge arrangement for comparing capacities with slight modifications. The connections are shown in the figure. E_1 and E_2 are the aluminium electrodes dipping into the solution S; E_1 is made so large in comparison with E_2 that the capacity measured is practically that of the small electrode alone; K is a three-point switch by means of which the cell is connected first to the battery P, in order to form the film on E_2, and then switched into the bridge for measurement.

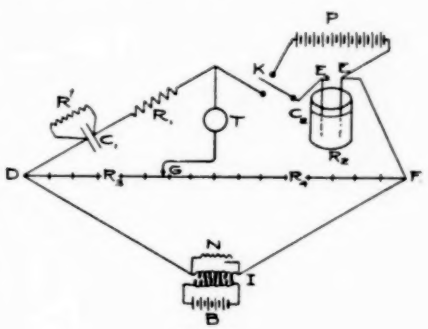

Fig. 1.

The capacity C_1 was a mica condenser of 0.5 Mf., or a paper condenser of 6.8 Mf. This paper condenser was marked by the maker 10 Mf., which was evidently its value by direct current measurement. Such condensers always give much lower values when measured by alternating currents; but their values are always consistent with one another, if a number of such condensers are compared with one another or with mica condensers.

R_1 is a variable non-inductive resistance in series with the condenser C_1, which is necessary to balance the conductivity of the solution. DGF is the bridge wire and T the telephone receiver. I is a small induction coil with automatic breaker, operated by the battery B; N is a shunt by means of which the current is kept small. Large currents give polarization effects which interfere with the accuracy of the bridge setting.

R' is a variable resistance which serves to balance the conductivity of the film itself. This resistance was found however to be unnecessary in most of the measurements of the capacity and was generally omitted.

With this arrangement of the bridge three conditions must be satisfied simultaneously in order that there shall be no current in the telephone, namely;

$$C_2 = C_1 \frac{R_3}{R_4}, \quad R_2 = R_1 \frac{R_4}{R_3}, \quad \text{and Film } R = R' \frac{R_4}{R_3}.$$

Using electrodes of a few square centimeters area, the position of the minimum is practically determined by the capacities. If the resistances are too far off from the proper ratios, the minimum is not sharp but with an approximate adjustment of the resistances it is possible to obtain a setting on the bridge certain to one millimeter.

These experiments were planned with the expectation that we could thus readily obtain an accurate measurement of the capacity and the resistance of the films at the same time. It was found however that the films most suitable for capacity measurements had a resistance so large as to have little effect on the sharpness of the telephone minimum, and it was accordingly decided to leave the resistance of the films for a later investigation, which is still in progress. Some interesting preliminary results on the resistance obtained are given further along in this paper.

The electrode E_2 on which the films were formed was a strip of sheet aluminium about 1 cm. wide and dipping into the solution from 1 to 4 cm. The other electrode was a sheet of aluminium about twenty times as large. In preliminary measurements a small electrode was also tried in place of the large one; a large sheet of lead was also substituted for the large aluminium electrode. The capacity calculated per cm.^{2} of one side of the electrode was the same for all three cases.

THE POLISH OF THE SURFACE.

The degree of the polish of the surface makes a considerable difference in the size of the capacity. Surfaces formed by cutting the aluminium under turpentine with a sharp instrument gave the smallest capacities. Sheets polished with emery cloth and sand paper gave larger values. At higher voltages the difference in the polish does not make so much difference. The variations in capacity with the polish of the surface are probably due to the actual differences in surface area. With the higher formation voltages the films are thicker, the uneven places are probably to some extent filled up and the capacity values consequently not so far apart. As the capacity values for surfaces cut under turpentine were practically the same as those of smoothly polished aluminium

as obtained from the manufacturers, the latter was used for the rest of the experiments. A series of measurements showing the amount of the variation with the differently polished surfaces is given in Table I.

TABLE I.

$(NH_4)_2CO_3$ Solution.		
Preparation.	Capacity in Mf. per cm.²	
	20 Volts.	100 Volts.
Cut under turpentine	0.33	0.0686
Emery cloth under turpentine	0.57	0.111
Emery cloth in air	0.70	0.129
Sand paper in air	0.65	0.129

TUBULAR ELECTRODES.

A number of observers have found that tubular electrodes, especially when water-cooled, are better for rectifying the current than the ordinary sheet electrodes. Fischer[1] found that water-cooled tubular electrodes, in sulphuric acid, insulated well at 100 volts and gave films several tenths of a millimeter in thickness. The tubular electrodes, however, even when cooled with water near 0°, give the same capacity values as the sheet electrodes. The thicker films found for sulphuric acid and sodium sulphate seem to be composed of two layers, the thicker part being a film of good conductivity, concerning which more will be said further on, under the discussion of the thickness of the films. The most noticeable difference between the water-cooled tube electrodes and those without water was in the rapidity with which the capacity increased after the formation current was turned off. In the first five minutes after turning off the current from the water-cooled electrode the capacity increased about ten per cent., while without water the increase was less than one per cent. in the same time.

TEMPERATURE.

A number of observers have found that the voltage at which the films begin to break down — the so-called critical voltage — decreases rapidly with the increase of the temperature. No corresponding variation in the capacity was found. The capacity re-

[1] Fischer, Zeit. für Eleck. Chem., 10, p. 869, 1904.

mained the same from 10° to 25° C., at least within the limits of experimental error, two to three per cent. After this had been established for three or four solutions, the remaining measurements were taken at room temperatures, probably varying between 15° and 25° C.

Time for the Formation of the Films.

The formation of the film is not by any means instantaneous. The current is at first large, but decreases rapidly, coming to practically constant values after some time. The decrease in the capacity as the current continues to run is likewise at first rapid and then slower, approaching a minimum value. This decrease in the capacity is not proportional with that of the residual current. For example in one case where the residual current was measured, the capacity decreased but six per cent. while the residual current changed in the ratio of six to one. Generally after five seconds application of the direct current the capacity was within a few per cent. of its minimum value. The time required to bring it within one per cent. of its minimum value varied largely with the voltage and somewhat with the solution. For 20 volts it was generally about five minutes and for 100 volts sometimes as much as twenty minutes. The values for the capacity given in this paper are minimum values, assuming that the minimum is attained when a further application of the formation current for five minutes gives a decrease of capacity of less than one per cent.

Capacity Measurements While the Polarizing E.M.F. is Still Applied.

Scott inserted the polarizing battery in the telephone arm of the bridge, and thus was able to take the capacity measurements while the polarizing current was acting. I made a comparison of this method with that as given above and found that the capacity measured with the current on, was the same as after it was off. The method as given above was accordingly used on account of its greater simplicity. The two methods give very different values for the film resistance, but more will be said about this in another paragraph.

Formation Voltage and Capacity.

After the above preliminary experiments, the first question considered was as to how the capacity changes with the voltage applied to form the film — which we shall speak of hereafter as the "formation voltage." Scott found that the capacity of aluminium in sulphuric acid decreased rapidly as the formation voltage increased, but as he did not use voltages higher than 1.75, he did not discover any simple relation between capacity and voltage. My first measurements were with a potassium alum solution and it was seen at once that for higher voltage the *capacity varies inversely as the formation voltage.* Measurements for two solutions are given in Table II. Similar results were obtained for a number of other solutions. The areas of the films whose capacities are given in this table were not measured.

Table II.

$HNaNH_4PO_4$ Solution.			$K_2Cr_2O_7$ Solution.		
Formation Voltage.	Capacity.	Product.	Formation Voltage.	Capacity.	Product.
I.	II.	I. × II.	I.	II.	I. × II.
20	1.60	32.0	10	3.8	38.0
30	1.11	33.3	20	1.95	39.0
40	0.83	33.2	40	0.95	38.0
50	0.64	32.0	81	0.48	38.9
60	0.54	32.4	90	0.42	37.8
71	0.46	32.7	100	0.38	38.0
80	0.40	32.0			
91	0.35	31.8			
100	0.32	32.0			

The variations of the product from a constant value are well within the experimental error. The natural explanation of this relation between the capacity and the formation voltage is that the thickness of the films is proportional to the formation voltage. During the progress of this investigation an article has been published by Fischer[1] in which he comes to the same conclusion in regard to the films formed in sulphuric acid; but the sulphuric acid films are quite different in character from those of most solutions as will be set forth below.

[1] Fischer, Zeit. für Elek. Chem., 10, p. 869, 1904.

THE CAPACITY IN DIFFERENT SOLUTIONS.

Experiments were next made to determine how the capacity might vary as the electrolyte was changed. The literature of the subject shows that with a change of the electrolyte there are large variations in the insulating power of the films and in the critical voltages. With sulphuric acid for instance, at room temperatures, the films break down between twenty and thirty volts, while for sodium potassium tartrate the critical voltage has been found to be at least as high as one hundred volts and for citric acid five hundred volts. Where chemical analyses of the films have been made they have been found to contain a considerable portion of the acid radical of the electrolyte. In view of these facts it was expected that each electrolyte would have, for any given formation voltage, its own individual capacity value, differing from that for other electrolytes, because of the difference in thickness and dielectric constant, which a difference in the chemical nature of film would probably cause. This expectation, however, was not realized, as will be seen from the figures given in Table III.

TABLE III.

Electrolyte.	Capacity in Mf. per cm.²	
	Formation Voltage 20.	Formation Voltage 100.
$(NH_4)_2CO_3$	0.34	0.069
$K_2Cr_2O_7$	0.35	0.069
$(CHOH)_2(CO_2)_2KNa$	0.35	0.069
$NaNH_4HPO_4$	0.34	0.072
$(CH_2)_2(COH)(CO_2H)_3$	0.33	0.070
Na_2SO_4	0.39	
H_2SO_4	0.50	

The above series of measurements was repeated several times. The variations seldom amounted to as much as three per cent. These small variations are easily accounted for when we take into consideration that with the voltmeter used errors in reading as large as two per cent., at twenty volts, might readily be made. The exact length of the film, determined simply from the depth immersed, could likewise not be measured with any great accuracy on account of capillary irregularities. The above figures show,

therefore, that within the experimental error at least, the capacity of the first five solutions, both at twenty and one hundred volts, is the same; and at the same time confirm the relation found before, *i. e.*, that the capacity is inversely proportional to the formation voltage.

The larger values found for sodium sulphate and sulphuric acid may be due to the fact that in these solutions the film dissolves more rapidly than in the others. While for the other solutions there was no decrease of the capacity with the film standing in the solution for five minutes after the formation current was turned off with sodium sulphate there was a small, and with sulphuric acid a large decrease in this time. Two sets of measurements showing the rapidity of this increase are given in Table IV.

TABLE IV.

H_2SO_4 Solution, Dilute.		
Seconds after Disconnecting the Formation Current.	Capacity (Size of Electrode not Measured).	
	Series I.	Series II.
20	0.400	0.393
80	0.452	0.427
170	0.65	0.62
230	0.93	0.89
290	1.09	1.07
350	1.20	1.16

FILMS IN FUSED SALTS.

Insulating films are also formed with fused salts as the electrolyte. In a mixture of fused sodium and potassium nitrates, the capacity was found to be smaller than in the water solutions. The capacity increased, however, so rapidly after the formation current was switched off, that no accurate determinations of the minimum value could be made. A series of measurements showing this rapid increase in capacity is given in Table V.

It is evident that the value obtained five seconds after the formation current is switched off is not the minimum value, but even this is only about one-sixth as large as water solutions give at the same voltage. The film evidently dissolves rapidly, making the film thinner and the capacity consequently larger.

TABLE V.

Fused KNO_3 and $NaNO_3$. Temperature 265° C. Form. Volts 20.	
Seconds after Formation Current was Disconnected.	Capacity in Mf. per cm.^{2}
5	0.06
60	0.16
120	1.05

The resistance of these fused salt films is much less than those of water solutions. While the resistance of the latter was so large that a resistance in parallel with the condenser had little effect upon the minimum, in case of the fused salts this parallel resistance must be adjusted somewhat carefully. On account of the rapid shifting of the position of the minimum no very accurate measurement of this resistance could be made but the largest value obtained was about 400 ohms for a surface of 15 cm.^{2} or 6000 ohms per cm.^{2}

THE RESISTANCE OF THE FILMS.

As was stated in a previous paragraph the resistance of the films formed at these voltages is so large as to have little effect on the bridge minimum. As these voltages seemed to be the most suitable for obtaining the comparative values of the compacity, it was decided to carry through the above measurements without attempting to obtain accurate values for the resistance at the same time, and to make an investigation of the resistance of the films later. The latter investigation is not yet completed but a few of the more striking results as determined from the preliminary experiments are included here.

1. The apparent resistance, as calculated from the residual direct current, does not increase at all in proportion with the decrease in capacity. If, as it seems reasonable to suppose, the decrease in the capacity during the formation of the film is proportional to the increased thickness of the film, the increase in apparent resistance is due to something else than mere increase of thickness.

2. The resistance as measured with the small alternating current in the bridge is much smaller than the apparent resistance as calculated from the size of residual current.

3. The resistance as measured in the bridge while the formation

current is still active (the arrangement of Scott) is only about one third as large as when measured after the direct current is taken off (the arrangement of the figure above). A discussion of the probable cause of this striking difference is deferred until some measurements of the resistance under other conditions are completed.

The Thickness of the Films.

If we knew the dielectric constant for these films we could of course calculate their thickness from their capacity. But even without such knowledge we can draw some conclusions as to the maximum and minimum values of the thickness from what we know as to the possible range of the dielectric constants, as well as to the relative thickness of the films under various conditions of formation.

In the first place it is to be noted that the films formed in sulphuric acid and sodium sulphate are very different in character from the other films. In the sulphates the whole film is evidently not insulating in charater; *but it seems as if we have an insulating film covered with a much thicker conducting one.* The reasons for this conclusion are as follows. Mott[1] and others had found that the films in sulphuric acid were much thicker than in other solutions. Mott says in one place that he found the thickness in sulphuric acid at twenty volts greater than that in a phosphate solution at 100 volts. In *apparent* contradiction to this I found the capacity of the sulphuric films to be somewhat larger than in any other solutions at corresponding voltages. If we use water cooled tubular electrodes it is easy to form films in sulphuric acid at formation voltages as high as 100, whose thickness is readily measured as it amounts to several tenths of a millimeter. Fischer[2] found the thickness of such films at 72 volts to be 0.03 cm. and I have found films formed at 100 volts to be between 0.03 and 0.04 cm. thick. The lowest values found for the capacity of such a film was 0.15 Mf. cm.[2] (Sheet aluminium with same surface polish gave 0.129 Mf.)[3] As the film stood in the solution the capacity increased very rapidly, becoming about ten times as large within a half hour, but there was no corresponding change in the thickness during that time.

[1] Mott, Elect. Chem. Ind., 2, p. 268, 1904.

[2] Fischer, l. c.

[3] This was in sodium carbonate solution, as given in Table I.

This alone would be enough to cause us to conclude that the visible film is not the same as the insulating film whose capacity is measured. The calculation of the dielectric constant which would be necessary in order that the whole film should have such a large capacity makes this conclusion doubly sure. Using the formula

$$C = \frac{KA}{4\pi d},$$

where C is the capacity, K the dielectric constant, A the area, and d the thickness, all expressed in c.g.s. units, for a capacity of 0.15 Mf. per cm. and a thickness of 0.03 cm., the dielectric constant would be over 50,000, which is of course out of the question.

In all the other solutions the films are not thick enough to be noticeable to the eye, and I know of no reason for supposing them to consist of anything else than a single insulating layer. It is safe to assume that the dielectric constant for this layer is somewhere between 1 and 80. Mott[1] and Zimmerman[2] conclude from their experiments that it is probably about 14. Table VI. gives the thickness of the films calculated from the capacity per cm.^{2} found above, assuming the dielectric constant to be 1, 10 and 100.

TABLE VI.

Calculated Thickness.

	$K=1$.	$K=10$.	$K=100$.
20 volts.....	2.5×10^{-7}	2.5×10^{-6}	2.5×10^{-5}
100 volts.....	12.5×10^{-7}	12.5×10^{-6}	12.5×10^{-5}

Zimmerman and Mott have estimated the thickness of such films from their interference colors. Mott estimates the thickness for 100 volts to be 10×10^{-5}. Zimmerman gives the thickness of a 100 volt film as 7.5×10^{-5}, but in another place speaks of a 100 volt film with a thickness of 2×10^{-5}.

[1] Mott, Elect. Chem. Ind., 2, p. 352, 1904.

[2] Zimmerman, Trans. A. E. S., 5, p. 147, 1904; 7, p. 309, 1905.

The Nature of the Films.

Mott[1] has advanced the hypothesis that the chemical nature and consequent thickness of the films are largely dependent upon the nature of acid radical of the electrolyte. Since, however, the capacity is independent of the electrolyte, this view, at least in so far as it has to do with the insulating film, is no longer tenable. The capacity being the same, we must conclude that the thickness and the dielectric constant are both independent of the electrolyte, or that in all the different solutions tried, the one varies exactly as the other. The latter might accidentally happen for two solutions but that it should be so for so many solutions is too improbable to be considered. If, however, we have the thickness and the dielectric constant both unchanged, it follows that we have practically the same chemical constitution for all these solutions. Of course there must be some chemical or physical differences in the films to account for the differences in conductivity and critical voltages. The results of this paper seem to fit in best with the theory that the films in all the water solutions are made up of aluminium hydroxide full of pores, and that the variations in the behavior of the films as we go from one electrolyte to another are due to the variation in the size or number of such pores.

Central University,
Danville, Ky., July, 1906.

[1] Mott, Elect. Chem. Ind., 2, p. 444, 1904.

INFRA-RED EMISSION SPECTRUM OF BURNING CARBON DISULPHIDE.[1]

BY W. W. COBLENTZ.

IT is becoming more and more a recognized fact that the infra-red spectrum is the seat of great disturbances which can be attributed to well-known groups of atoms or "ions." The pioneers in this field of investigation were Ångström and Julius. Their interest in the subject dates back to the time when rock salt first became recognized as a means for producing a heat spectrum. The dispersion of rocksalt was then undetermined beyond 5 μ, and in order to express their emission and absorption bands in wave-lengths they adopted a tentative method of extrapolation, which, since then, has been found to be erroneous. In the meantime, data on infra-red spectra have continued to accumulate, which are often in violent disagreement. For example, carbon disulphide is variously quoted as having a band at 6.7 to 8.4 μ while the true value is about 6.8 μ.

During the past few years the writer has attempted to determine the values of the maxima of absorption and emission as accurately as possible in absolute value of wave-lengths, and thus bring a little harmony out of this chaos. This means repeating part of the work in order to get a check upon the extrapolation. One of the most interesting pieces of work of this type is that of Julius [2] who found the emission spectra of gases during combustion. It contains a very considerable amount of careful work, certain parts of which appear to have gone quite unnoticed by later investigators. It is of no little interest for it contains evidence of emission bands farther in the infra-red than subsequent work, along other lines, has been able to show. These bands belong to the acid elements and appear at low temperatures, *i. e.*, they do not appear in spark (and arc?) spectra. This is just the opposite of what the writer found for the basic elements (metals) in which no emission bands were found beyond 2 μ.

[1] Extracts from a memoir submitted to the National Bureau of Standards for publication.

[2] Julius, Licht und Wärmestrahlung Verbrannter Gase, Berlin, 1890.

Perhaps this may eventually give us some clue to the mechanism of radiation. We have two sharp distinctions between the acid and the basis elements. The metals have selective absorption in the short wave-lengths, are opaque to infra-red rays, and no emission lines have been found beyond 2 μ. In fact, according to Pflüger's[1] work the maximum of the emitted energy lies in the short wave-lengths beyond the visible spectrum. On the other hand, the acid elements have bands of selective absorption throughout the spectrum and have emission bands extending far into the infra-red, which generally coincide with the marked absorption bands. The question of the coincidence of these emission and absorption bands in CS_2 led the writer to undertake the present work.

A previous examination of the absorption spectra of gases[2] showed very marked bands in SO_2 which were in quite close coincidence with the emission lines of the products of combustion of carbon

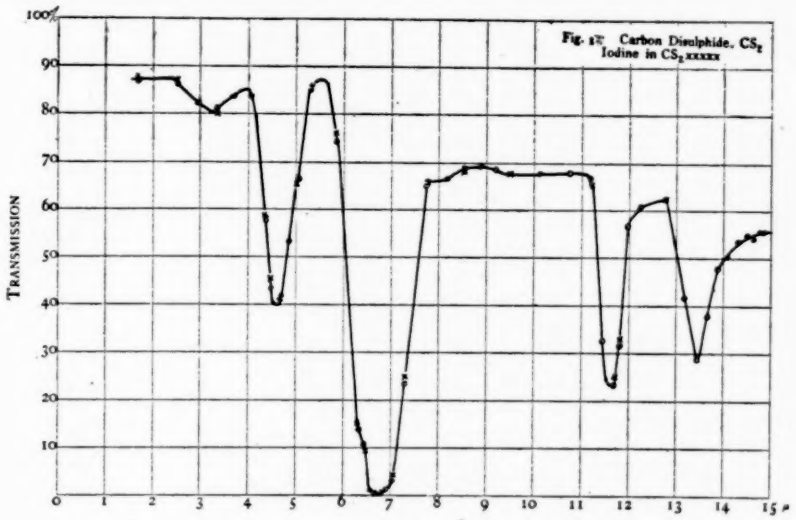

Fig. 1.

disulphide, as given by Julius. The transmission spectrum of CS_2, Fig. 1, has a very large absorption band at 6.8 μ (opacity from 6.6 to 7.0 μ) and smaller bands at 4.6 and 11.65 μ, while SO_2, Fig. 2, has a very large band at 8.7 μ, a somewhat narrower band at 7.4 μ

[1] Pflüger, Ann. der Phys. (4), 13, p. 890, 1904.
[2] PHYSICAL REVIEW 20, 273, 1905.

and several small bands; H_2S has a series of small bands which need hardly be considered in the question of the combustion products of CS_2. In Fig. 3 is given the emission curve of burning CS_2. In curve *a* the maximum at 4.35 μ is drawn to the same scale as the rest of the curve. In curve *b* the bands at 6.75 and 7.45 μ have

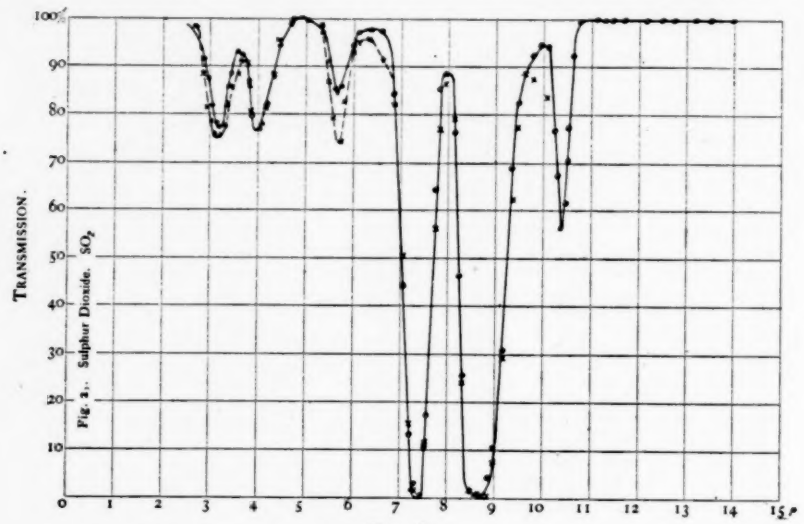

Fig. 2.

been magnified ten times to bring out the sharpness of the maxima. In the present examination the lower part of the flame was examined. The lamp consisted of a tin lubricating-oil can, the neck of which was 5 cm. long, to prevent heating the CS_2 and thus avoid an explosion. Julius (loc. cit.) examined the upper and the central parts of a CS_2 flame and found that for the central region the maximum at 6.75 μ is more intense than the one at 7.45 μ while for the upper region the 7.45 μ band is the more intense. This is to be expected for the 6.75 μ band is evidently due to hot CS_2. In the lower part of the flame the combustion is incomplete and hence the hot vapor ought to be more intense than nearer the top of the flame. In the present examination the lower part of the flame was used, and the ratio of the intensities of these two bands is still greater than that found by Julius; here the ratio is 34 to 73 while Julius found a ratio of 16 to 22 for the central part of the flame and a ratio of 11 to 8 for the top.

The band at 7.4 μ is in common with the absorption band of SO_2 and since Julius found this band also in burning sulphur, it no doubt belongs to this gas. Then the interesting question arises, "Why is there no emission band at 8.7 μ?" The question must be left unanswered. It is interesting to note, however, that the 8.7 μ band is found in H_2SO_4, and in sulphates, and appears to belong to the SO_4 ion, while another band found in SO_2 gas, at 10.37 μ occurs in fuming H_2SO_4 and has been attributed to SO_3, by Pfund.[1]

The bands at 2.7 μ and 4.35 μ are in common with the emission

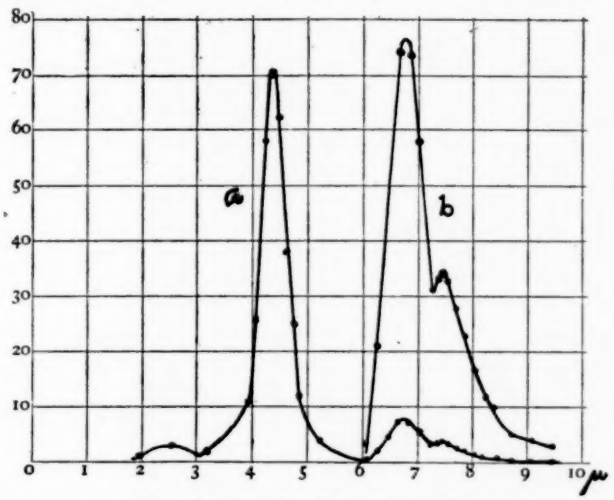

Fig. 3. Emission Spectrum of CS_2.

bands of CO_2 and are no doubt due to the combustion of the lamp-wick.[2] This is one of the few examples of the emission of a heated gas during the process of combustion. Water vapor and CO_2 are other examples studied by Rubens and Aschkinass. Kayser in his Spectroscopy very aptly remarks that the emission band of methane, CH_4, at 3.3 μ has never been observed in a flame. This is a very weak absorption band, however, and for this reason might not appear in emission, just as was found for the 4.6 μ band of CS_2. The 6.75 μ band which coincides with that of CS_2 was ascribed to COS by Julius who records its maximum in wave-lengths at 8.48 μ. The 7.45 μ band was thought to be at 10.01 μ. The emission spectra

[1] Pfund, Astrophys. Jour., 24, p. 19, 1906.

[2] The combustion of CS_2 gives CO_2 and SO_2.

of H_2O and CO_2 have been redetermined by others and need not be mentioned here. It will be sufficient to add that for CO_2 the maximum of emission depends upon the temperature. Whether this is true of the SO_2 bands remains undetermined, but it is hoped to examine this point in the near future. If the shifting of the CO_2 band is really due to dissociation into CO, as experiments seem to indicate,[1] then one would hardly expect a similar shift for SO_2. The only other emission band that needs correction is that of HCl at 3.68 μ. A more probable value is 4.05 μ which is close to the HCl band, found by Ångström and Palmer[2] at 3.41 μ. The corrected value is 3.98 μ.

[1] PHYSICAL REVIEW 221, 1906.

[2] Aengström and Palmer, Ofversigt Kongl. Vet. Akad., No. 6, p. 389, 1893.

ON THE IONIZATION OF FUSED SALTS.[1]

By H. M. Goodwin and H. A. Wentworth.

Contributions from the Research Laboratory of Physical Chemistry, No. XII.

THE following investigation was undertaken in the spring and summer of 1905 in the hope of contributing something to our knowledge of the applicability of the well established laws of dilute solutions to fused mixtures, and possibly of throwing some light on the question of the constitution of salts in the state of fusion.

Investigations bearing upon the determination of the degree of dissociation of fused salts have already been published, but the results obtained are meagre and cannot be regarded as conclusive. This is chiefly due to the peculiar difficulties inherent in the problem which are not encountered in aqueous or other solutions at ordinary temperatures. Aside from the obvious experimental difficulties incident to working at high temperatures and with vessels unattacked by fused salts, are the difficulties arising from the fact that pure fused salts are in general such excellent electrolytic conductors; although their conductivities may now be determined with precision,[2] transference experiments in them are impossible, since no concentration changes occur at the electrodes during electrolysis, and data on the absolute velocity of migration of ions in such conductors are at present entirely wanting. Direct velocity experiments with fused electrolytes have been recently attempted in the electrochemical laboratory of the Institute, but the exceeding difficulty of the problem has prevented as yet the obtaining of any satisfactory results. With solutions of one salt in another the relations are far more difficult of analysis than in aqueous solutions where the conductivity of the solvent may practically be neglected. Here, to be sure, transference experiments are possible and Lorenz[3]

[1] This research was carried out under a grant from the Wm. E. Hale Research Fund, to the trustees of which grateful acknowledgment for the aid furnished by them is hereby made.

[2] An investigation on this subject is now being carried on by one of us, the results of which will be published shortly.

[3] Zeit. für Electrochemie, 10, 630, 1904.

has made a first attempt in this direction with solutions of lead chloride in potassium chloride, his results pointing to more complex relationships than had been supposed.

The most promising method of attacking the problem of the dissociation of one fused salt in another seems at present to lie in the application of some selective ion-phenomenon, *i. e.*, in measuring some quantity which depends, so far as we know, on the presence of a specific molecular or ionic complex. Of the quantities suitable for this purpose the electromotive force of certain voltaic cells composed of fused mixtures lends itself best for determining specific cation concentrations, provided that Nernst's theory of the voltaic cell is applicable to combinations of this type. It is upon the results of electrometric experiments that most previous work on this subject has been based and upon which the present investigation rests.

The first experimental work bearing upon the problem under consideration was carried out by Gordon[1] and consisted of the measurement of the electromotive force of concentration cells of the type

$$\mathrm{Ag}\left|\begin{array}{c}c_1,-\mathrm{AgNO_3}\\ \text{in}\\ \mathrm{KNO_3+NaNO_3}\end{array}\right|\left|\begin{array}{c}c_2,-\mathrm{AgNO_3}\\ \text{in}\\ \mathrm{KNO_3+NaNO_3}\end{array}\right|\mathrm{Ag},$$

equimolecular mixtures of sodium and potassium nitrates being used to give a solute of low melting point. The concentration of the silver nitrate was varied from 0.1 to 100 per cent. On the assumptions, first, that Nernst's formula applies to cells of this type, second, that the electrolytic solution pressure of silver is independent of the solutions in question, and third, that the dissociation of a 0.1 per cent. solution of silver nitrate may be regarded as complete, Gordon calculated that the dissociation of a 50 per cent. solution of silver nitrate was 69 per cent. at 236° C., and a 100 per cent. solution, *i. e.*, pure silver nitrate, was 58 per cent. dissociated. While the experimental results of this investigation which was carefully carried out may be accepted, certain of the above assumptions on which the computations rest render the conclusions open to question.

[1] Gordon, Zeit. f. Phys. Chem., **28**, 302, 1896.

More recently the same problem has been taken up from a slightly different standpoint by Lorenz and his pupils at Zurich. Following an extended series of investigations[1] on decomposition potentials and on the electromotive force of cells composed of fused salts, Suchy[2] in 1901, from measurements of cells of the type computed

$$\mathrm{Pb} \;\big|\; \mathrm{PbCl_2} \;\big|\; \begin{matrix}\mathrm{AgCl}\\ \text{in}\\ \mathrm{LiCl + KCl}\end{matrix} \;\big|\; \mathrm{Ag},$$

the dissociation of silver chloride in a lithium and potassium chloride mixture as follows:

Two cells of the above type differing only in the concentration of silver chloride were measured at temperatures varying from 500° to 650° C. The concentrations chosen were 1.858 n — AgCl and 0.035 n — AgCl respectively. If the observed electromotive force of these cells at corresponding temperatures be E_1 and E_2 respectively, and Nernst's formula be assumed to hold for each, then

$$E_1 - E_2 = \frac{RT}{2F} ln \frac{P_{Pb}}{p_{Pb}} - \frac{RT}{F} ln \frac{P_{Ag}}{p_1} - \frac{RT}{2F} ln \frac{P_{Pb}}{p_{Pb}} + \frac{RT}{F} ln \frac{P_{Ag}}{p_2}$$

or

$$E_1 - E_2 = \frac{RT}{F} ln \frac{p_1}{p_2},$$

$$= \frac{RT}{F} ln \frac{c_1}{c_2},$$

in which c_1 and c_2 are the *silver-ion* concentrations at the two electrodes respectively. If $E_1 - E_2$ be measured and the value of c_1 known or assumed, c_2 may be calculated. Suchy assumed that the 0.035-normal solution of silver chloride was completely dissociated, from which it followed that the computed dissociation of the 1.8-normal solution of silver chloride at 600° was 33 per cent. From measurements of a similar cell in which pure silver chloride replaced the silver chloride solution at one electrode, values for the dissociation of the pure salt at various temperatures were also computed. They varied from 17 per cent. at 520° to 60 per

[1] Czepinski, Zeit. für anorg. Ch., **19**, 208, 1899. Lorenz, ibid., **19**, 283, 1899. Weber, ibid., **21**, 305, 1899. Lorenz, ibid., **22**, 241, 1900.

[2] Suchy, Zeit. für anorg. Ch., **27**, 152, 1901.

cent. at 730°. These results are regarded by the author as only first approximations. They rest on the following assumptions: (1) That a 0.035-normal solution of silver chloride in a chloride mixture is completely dissociated (questioned by Lorenz himself)[1]; (2) that the electrolytic solution pressure of silver may be regarded as independent of the solvent for solvents as widely different as fused pure silver chloride and a mixture of lithium and sodium chlorides (see discussion by Bodlander and Lorenz)[2]; (3) that the potential difference at the liquid junction is negligible — an assumption probably well founded; (4) that the effect of a common anion in the solvent on the dissociation of the solute may be neglected. This last assumption seems to have been entirely disregarded in all previous computations of the kind under discussion.

In concluding this resumé of previous work mention should be made of one other method of computation of the order of magnitude of the dissociation of a fused salt suggested by Abegg,[3] based on the assumption that the decomposition voltage of an ion is independent of the medium in which it is dissolved. Thus, if 0.7 volt be taken as the decomposition voltage of silver chloride, he computes that the silver ions in fused silver chloride must have a concentration of about 0.01 normal.

Beyond these investigations little has been accomplished in determining the degree of dissociation of fused electrolytes. It was with the hope of obtaining some further data which might contribute towards the elucidation of this problem that the following investigation was undertaken, particular attention being directed to the possible effect of the dissociation of the solvent on the dissociation of the solute.

Apparatus and Method.

Furnaces. — For carrying out the experiments described below, we required two furnaces, both of which were of the electrical resistance type. The principal furnace, in which the measurements were made, was constructed of four porcelain tiles forming the inside lining of a rectangular iron box. Through holes which extended from the top to the bottom edges of the tiles, were threaded

[1] Zeit. für Anorg. Chem., 32, 246, 1902.
[2] Zeit. für Anorg. Chem., 31, 389, 1902; 32, 235, and 239, 1902.
[3] Zeit. für Chem., 5, 353, 1899.

about twelve feet of No. 21 (B. & S.) platinum wire. The outside of the furnace was covered with asbestos to prevent radiation as far as possible.

Within the furnace was placed a box of thin cast iron, the approximate inside dimensions of which were 5.7 cm. × 3.2 cm. × 6.4 cm. deep. This formed the receptacle for a bath consisting of a mixture of fused sodium and potassium nitrates with a small amount of silver nitrate added. The composition of this bath was not determined exactly, a mixture of nitrates being used simply to obtain a low melting point. Gordon found in his experiments that the composition of the intermediate electrolyte, connecting the halves of a concentration cell, had no effect on the results. The bath was well stirred by a glass stirrer driven by a small electric motor, and was kept covered with several sheets of mica to prevent excessive radiation. The surface of the liquid seemed to be the greatest source of heat loss, but for temperatures below 500° C. this was not excessive, when the apparatus was well shielded from air currents. The temperature was regulated by an adjustable rheostat connected in series with the furnace, and could be maintained constant to within 2° C., as long as desired.

Another large platinum resistance furnace was used for melting the salts in the proper cells prior to plunging them into the above described nitrate bath for measurement. This was constructed by winding about three meters of No. 28 platinum wire on a clay cylinder, 25 cm. high by 8 cm. diameter, previously coated with pure magnesium oxide ; the cylinder was then heat insulated by packing it with a layer of magnesia ten centimeters thick. It was found convenient to first melt the salts in this furnace, as the glass vessels usually cracked if they were put directly into the fused salt bath. Both furnaces were run on the 110 volt D.C. circuit and the heating current adjusted by rheostats.

Temperature Measurements. — Temperatures were measured by a platinum-rhodium junction. The junction was inserted in the bath between the two parts of the vessel containing the fused salts to be measured. The stirring was, however, so effective that all parts of the bath were always practically at the same temperature.

The temperatures were deduced from deflections of a sensitive

d'Arsonval galvanometer of the Le Chatelier type. In order to prevent changes in the sensitiveness of the galvanometer due to temperature changes in the room from time to time, the galvanometer was enclosed in a small air thermostat built up of asbestos and magnesia board, the mirror being observed through a small window. As great precision in temperature regulation was unnecessary in this investigation, the sensitiveness of the galvanometer was so adjusted that one degree temperature change gave a deflection of about one scale division. The instrument could easily be read to one half of a division, hence temperatures could be measured to one half a degree without difficulty, a precision greater than the work really demanded. The junction was calibrated every few days throughout the work, and the calibration was found to remain very constant. The following points were taken for calibration : water, 100°, naphthalene 218°, benzophenone 306°, sulphur 445°. The cold junction was kept always at zero degrees in an ice mixture.

Potential Measurements. — Potentials were measured by the usual Poggendorf compensation method, by balancing them against a fall of potential along a calibrated slide wire bridge. The voltages were repeatedly checked by comparison with a standard Weston cell and a Clark cell standarized at the Reichsanstalt. A Lippmann electrometer sensitive to 0.0003 volt was used as indicating instrument. All circuits were carefully insulated, and to prevent any possible leakage from the 110 volt heating circuit, the latter was opened before each potential measurement.

Form of Cell. — The cells were made of Bohemian glass. As this does not begin to soften until about 800° C., it was sufficiently hard for all temperatures used in our experiments, which did not exceed 450°. For the first portion of the work, H-tubes, 9 cm. in length and 6.4 mm. diameter, having an inclined cross arm of small tubing were used. This cross arm was filled with a plug of prepared asbestos which was found to completely prevent diffusion of the solutions in the two sides. The liquid-liquid contact came well within the boundaries of the plug. The H-tubes were immersed to within 3 cm. of their top, in the fused nitrate bath, their contents being thus entirely insulated from the material of the bath. The greater portion of our work was carried out with cells of this kind.

Since, however, these were found to crack rather easily, the following modified form of cell was used in some of the later work. In this the two electrodes were contained in separate glass tubes drawn down at the end, as in the experiments of Suchy and others, electrolytic connection between them being made by means of the liquid constituting the bath. The potentials obtained in this way were found to check exactly those obtained with the closed tubes. The tubes were suspended in the bath so that the level of the liquid within and without was the same. To prevent convection and diffusion, the ends were closed with asbestos plugs.

The electrodes consisted of fine platinum wires heavily plated with pure silver. These electrodes were scraped and washed perfectly clean before using. Similarly prepared electrodes gave concordant results. The electrodes were carefully suspended in the molten salts and served also the purpose of stirring the latter.

Preparation of Salts. — The following salts were used in our experiments: sodium, potassium, and silver nitrates and silver chlorate. The sodium and potassium nitrates were recrystallized until free from chlorides; "C.P." silver nitrate was recrystallized twice. Silver chlorate was made by precipitating barium sulphate from a hot saturated solution of silver sulphate, with barium chlorate, the latter being first freed from all traces of chloride by crystallization. The silver chlorate, was then separated from the slight excess of barium chlorate in the filtrate, by fractional crystallization. Silver chlorate separates out as beautiful, long, fine, shiny needles, which are easily dried.

Preparation of Mixtures. — All salts were first fused and cooled in a desiccator before the final weighing. The mixtures were then made up in the following manner: The pure fused salts were weighed out in the desired proportions. The sodium or potassium nitrate, as the case might be, was then fused, and while just above its melting point, the silver salt was added. This procedure was followed in order to prevent any reduction of the silver salt by over heating before or during the process of fusion. It was found that the salts of the silver, when once in solution, could be kept fused far above their decomposition points without any apparent reduction. For example, silver chlorate melts at about 230° and decomposes

at about 270°; but, if dissolved in 95 per cent. of sodium nitrate, it can be carried above 350° without any apparent decomposition. After adding the silver salt, the mixture was thoroughly stirred and allowed to cool, vigorous stirring being continued as long as possible. When cold the mixture was broken up and very finely ground in a mortar until different samples gave the same analysis. If the mixtures were allowed to cool without continual stirring, a hard crystalline mass was obtained, which varied in appearance as the composition changed. The mixtures of sodium and silver nitrates solidified in a coarsely crystalline mass which could be broken up easily. With the mixtures of potassium and silver nitrates, however, the texture was fine, and as the concentration of the silver nitrate approached 50 per cent. the mass became extremely hard, resembling marble in appearance. The same was true of silver chlorate, although the mass became very hard with only a small percentage of silver chlorate added.

With the higher concentrations of silver nitrate, the salts were analyzed both before and after the measurements, but with mixtures containing only a very small percentage of silver, this procedure was not practicable. For these mixtures the salts were dried carefully and the proportions made up by weight, the conditions tending to cause a reduction of the silver salt being eliminated so far as possible.

Procedure. — The general procedure for making a potential measurement was as follows: The two mixtures to be investigated were put into their containing vessels or cells and placed in the air-bath furnace to fuse, this bath being kept just above the melting point. As soon as the salts had melted, the vessels were quickly transferred to the nitrate bath of the main furnace, which had previously been brought to the desired temperature. The electrodes were then inserted, the mixtures well stirred, and the measurements begun. As a rule the electromotive force increased rapidly at first, reached a maximum, remained constant for a time and then decreased slowly. The time required for the electromotive force to reach a constant value varied somewhat with each type of cell. The mean of a series of readings taken over an interval of five to ten minutes after the electromotive force had become essentially constant was taken as the observed electromotive force of the cell.

Density Determinations. — In order to calculate the concentration of the various solutions used, in terms of their normality, the density of the salt mixtures had to be determined. The following method was used: a cylinder of Brazilian quartz was cut from a crystal parallel to the principal axis, and used as the sinker of a Westphal balance, a set of weights being adjusted so as to correspond to its volume. A correction for its expansion with the temperature could be made, as the coefficients of expansion along and at right angles to the principal axis of quartz are known. The sinker was suspended in the molten salt the density of which was desired. This was fused in a large platinum crucible placed in the larger electric furnace. In certain experiments where the highest precision attainable was desired the natural quartz sinker was replaced by a fused quartz cylinder, this material being preferable on account of its very small expansion coefficient.

The densities of mixtures of silver and sodium nitrates were all measured, as well as those of a few mixtures of silver and potassium nitrates. For solutions of silver chlorate in sodium nitrate the densities were not measured, but estimated, it being assumed that for a given concentration the same change in density from that of the pure solute (sodium nitrate) occurred, as in the case of silver nitrate solutions. This seemed justified, as the densities of pure silver nitrate and of pure silver chlorate were found to be very nearly the same, and the concentration of all solutions investigated was not greater than 5 per cent. This assumption does not introduce an appreciable error, compared with the precision of other factors of the work.

The data on the density of the fused salts used in this research are not inserted in this paper as they are to be published shortly in connection with the research before mentioned on the conductivity of fused salts.

Investigations of Cells of the Type

$$\mathrm{Ag}\,\Big|\,\underset{c_1}{\mathrm{AgNO_3\ in\ N\ \ O_3}}\,\Big|\,\underset{c_2}{\mathrm{AgNO_3\ in\ NaNO_3}}\,\Big|\,\mathrm{Ag}.$$

The first series of experiments were carried out on cells of the above type which are identical with those investigated by Gordon,

except that in his cells a mixture of sodium and potassium nitrate was used as solvent. While Gordon in his experiments chose his solutions of concentrations from 0.1 to 100 per cent. silver nitrate, we have extended the experiments to diluter solutions to which the assumptions underlying the application of Nernst's formula may with more probability be assumed to hold. Experiments have also been repeated with concentrated solutions in order to determine the limits within which Nernst's formula applies.

For dilute solutions the electromotive force of the above cell may be written

$$E = \frac{RT}{F} ln \frac{(Ag)_1}{(Ag)_2}, \qquad (1)$$

where $(Ag)_1$ and $(Ag)_2$ are the concentrations of the silver ions in the two solutions respectively. Now from conductivity measurements of pure fused nitrates, it is certain that both the sodium and silver nitrate must be more or less dissociated. If we assume that dissociation in a fused salt takes place as in aqueous solutions, *i. e.*, in the case of sodium nitrate according to the equation

$$NaNO_3 = \overset{+}{Na} + \overset{-}{NO_3},$$

and if the mass action law applies to the equilibrium of this reaction, then at any given temperature

$$\frac{(Na) \times (NO_3)}{(NaNO_3)} = \text{constant},$$

where the symbols in parenthesis represent the concentrations of the respective ions and undissociated molecules. If to this nitrate as solvent, silver nitrate be added in such quantities that the resulting solutions are so dilute with respect to silver nitrate that the number of NO_3 ions per unit volume arising from its dissociation may be neglected compared with the number of NO_3 ions resulting from the dissociation of the solvent, then, over the range of concentrations to which this assumption applies, the total number of NO_3 ions present may be regarded as practically constant, *i. e.*, we may assume $(NO_3) = \text{const.}$, and hence also $(Na) = \text{const.}$ If further the silver nitrate dissolved in sodium nitrate dissociates according to the equation

$$AgNO_3 = \overset{+}{A}g + \overset{-}{N}O_3$$

we have for a given temperature

$$\frac{(Ag) \times (NO)_3}{(AgNO_3)} = \text{constant.}$$

Since by supposition (NO_3) = constant it follows that

$$\frac{(Ag)}{(AgNO_3)} = \text{constant,}$$

from which by proportion we obtain

$$\frac{(Ag)}{(Ag) + (AgNO_3)} = \text{constant.}$$

But $(Ag) + (AgNO_3) = c$ the total concentration of silver nitrate dissolved in the sodium nitrate; hence for solution (1) we have

$$\frac{(Ag)_1}{c_1} = \text{constant,}$$

and for solution (2)

$$\frac{(Ag)_2}{c_2} = \text{constant,}$$

therefore,

$$\frac{(Ag)_1}{(Ag)_2} = \frac{c_1}{c_2},$$

or in other words as long as the solutions of silver nitrate in a nitrate are dilute, the ratio of the silver ion concentration at the two electrodes is equal to the ratio of the total silver nitrate concentration of the solution. The formula for the electromotive force may therefore be written

$$E = \frac{RT}{F} ln \frac{c_1}{c_2} \qquad (2)$$

and hence values of E computed on the basis of Nernst's theory and *total* concentrations of silver nitrate should agree with experimental results if the mass action law applies to cases like the above, and this will be true whether the dissociation of the silver nitrate is great or small. To assume complete dissociation for the solute at any given concentration because of a close agreement between observed values and values computed by the above formula, as was done by Gordon in his investigation is, therefore, open to question.

We have tested formula (2) over a range of concentrations with the results given below.

TABLE I.

$AgNO_3$ in $NaNO_3$.

Equivalent Concentration of $AgNO_3$ at 400° C.		Temperature.	E (Observed).	$E=\frac{RT}{F}\ln\frac{c_1}{c_2}$ (Calculated).	Δ Difference.
c_1	c_2				
0.00986	0.06206	350	−0.1014	−0.0986	+0.0028
0.00986	0.06206	350	−0.0996	−0.0986	+0.0010
0.00986	0.1220	337	−0.1335	−0.1320	+0.0015
0.06206	0.1220	349	−0.0370	−0.0362	+0.0008
0.5565	0.1220	340	+0.0781	+0.0800	−0.0019
0.5565	0.00986	340	+0.2094	+0.2130	−0.0036
0.5250	0.04999	329	+0.1230	+0.1220	+0.0010

In Table I. are given the results of experiments made with the diluter solutions. In the first and second columns are given the concentrations of the silver nitrate solutions expressed (throughout) in equivalents per liter and calculated from measurements of their density and percentage composition ; in the third column is given the temperature of the cell at the time of the measurement ; in the fourth column the observed electromotive force (taken plus from solution (1) to (2)) ; in the fifth column, the electromotive force calculated by formula (2), and in the last column the difference between the observed and calculated *numerical* values.

It will be seen that up to half normal solutions the agreement is practically complete, the experimental error in cells of this type being from 0.001 to 0.002 volt.

Replacing the sodium nitrate by potassium nitrate as a solute we obtained an equally good agreement between calculated and observed values of the electromotive force. Thus for a cell in which $c_1 = 0.3205$, $c_2 = 0.0480$, $t = 347°$ C., the observed value of $E =$ 0.1003 volt while the computed value was 0.1008 volt. Over this range of concentrations therefore, formula (2) holds valid.

When, however, the concentration of the silver nitrate exceeded about 0.5 normal the deviations between observed and calculated values became increasingly greater and always in the same direction. This will be seen from Table II. These measurements were all carried out at approximately 350°. The concentrations (first and

TABLE II.

$AgNO_3$ in $NaNO_3$. Temperature = 350° C.

Equivalent Concentration of $AgNO_3$.		E (Observed).	$E=\frac{RT}{F} ln \frac{c_2}{0.01}$ (Calculated).	$E=\frac{RT}{F} ln \frac{c_1}{0.01}$ Reduced.	$\frac{c_1}{0.01}$	$\frac{(Ag)_1}{(Ag)_{.01}}$
c_1	c_2					
0.531	0.0507	0.1230	0.0875	0.2105	53	55
0.531	0.0572	0.1160	0.0908	0.2068	53	53
1.065	0.0421	0.1660	0.0752	0.2412	107	100
1.780	0.1094	0.1412	0.1258	0.2670	178	159
2.345	0.0643	0.1812	0.1000	0.2810	235	199
4.63	0.0418	0.2313	0.0758	0.3071	463	331
7.38	0.684	0.1066	0.2213	0.3279	738	528
13.20	0.0668	0.2502	0.1003	0.3505	1320	764
22.48[1]	0.273	0.1963	0.1957	0.3720	2250	1100

second columns), were as before computed from density determinations of the solutions in question. The third column contains the mean value of the observed electromotive force. In the fourth column are given the computed values of the electromotive force of similar cells, the diluter solutions of which are always 0.01 normal, and the more concentrated solutions of which are c_2 respectively. As c_2 is in every case (except one, 0.68) less than 0.5 normal, these values may be accepted as correct as just shown by the above results in Table I. If therefore these electromotive forces be added to the corresponding observed value of E for cells in which c_2 is the diluter concentration, we obtain the electromotive force of cells in each of which the diluter solution is 0.01 normal and the more concentrated solution c_1 respectively. This assumes that the liquid junction potentials are negligible. All cells may thus be referred to a common concentration, namely 0.01 normal. The computed value of the ratio of the concentration $c_1/0.01$ for each of the cells is given in column six, while the ratio of the silver ion concentration $(Ag)_1/(Ag)_{0.01}$ as computed from formula (1) is given in the last column. It is seen that in passing from solutions 0.5 normal those of greater concentration the computed and observed ratios begin to deviate with increasing rapidity, the ratio of the silver ions being less than the ratio of the total silver nitrate concentrations. This is what theory would lead us to expect as soon as the concentration of the NO_3 ions coming from

[1] Pure silver nitrate.

the silver nitrate itself is no longer negligible compared with the concentration of NO_3 in the solute. Until however, we have further data on the degree of dissociation of the latter and are thereby in a position to compute its effect on the dissociation of an added nitrate, dissociation values computed from the last two columns of Table II., can have but little significance.[1]

CELLS OF THE TYPE

$$Ag \left| \begin{matrix} AgClO_3 \text{ in } NaNO_3 \\ c_1 \end{matrix} \right| \left| \begin{matrix} AgClO_3 \text{ in } NaNO_3 \\ c_2 \end{matrix} \right| Ag.$$

We next investigated a concentration cell in which the solute and solvent had no ion in common. Silver chlorate was chosen as solute and sodium nitrate as solvent. For this cell, the conclusion arrived at in the discussion of the preceding cells, namely that for dilute solutions the ratio of Ag-ion concentration and total concentration at the two electrodes is the same, no longer holds; for an interchange of ions between solvent and solute probably takes place according to the reaction

$$AgClO_3 + NaNO_3 = AgNO_3 + NaClO_3$$

some undissociated silver nitrate and sodium chlorate being formed. If the amount of undissociated silver nitrate thus formed is appreciable, the concentration of silver ions will not be equal simply to the concentration of $AgClO_3$ multiplied by its percentage dissociation, but, depending upon the quantity of undissociated silver nitrate formed will be less than this. We should expect, therefore, that the computed ratio of the silver ion concentration in a concentration cell of this type would not be equal to the concentration ratio of the dissolved salt even in dilute solutions, but would be less. This was in fact found to be the case as the results in table III. clearly show. Here it will be seen that all values of the electromotive force calculated on the basis of the formula $E = \frac{RT}{F} ln \frac{c_1}{c_2}$, where c_1 and c_2 are the total concentrations of the solutions, are in every case *greater* than the ob-

[1] Since this paper went to press, the third part of Professor Lorenz's work on the "Elektrolsye Geschmolzener Salze" has reached me and I note that he has come to this same conclusion.

TABLE III.

$AgClO_3$ in $NaNO_3$.

Equivalent of Concentration of $AgClO_3$.		Temperature.	E (Observed).	$E=\frac{RT}{F}\ln\frac{c_1}{c_2}$. (Calculated).	Δ Difference.
c_1	c_2				
0.0756	0.0358	349	0.037	0.040	−0.003
0.0756	0.0235	332	0.053	0.060	−0.007
0.0756	0.0235	345	0.053	0.061	−0.008
0.294	0.0235	345	0.116	0.136	−0.020
0.294	0.0235	357	0.116	0.136	−0.020
0.493	0.0756	356	0.095	0.101	−0.006

served values, by amounts considerably in excess of the experimental error. Over this same range of concentration, with silver nitrate as solute, the agreement between observed and calculated values was complete. The difference between observed and computed values indicates either that the dissociations of silver chlorate changes (diminishes) rapidly with increasing concentration, or that the effect of the reaction between solvent and solute results in the formation of a very considerable amount of undissociated silver salt. In either case it seems reasonable to conclude that the dissociation of the chlorate is by no means complete or even approaching 100 per cent. at the concentrations investigated.

In view of the present state of our ignorance of the absolute value of the dissociation of any fused salt in even dilute solutions, it seems to us premature to attempt to conclude more from the above experiments than that Nernst's theory of the cell and the laws underlying the mutual effect of one ionized salt on another hold for salts in the molten state as well as in aqueous solution. These conclusions seem, however, well established by the above experiments, and hence the great importance which must be attached to the effect of the ionized portion of the solvent on the ionization of the solute in cases of fused inorganic mixtures. The analogue in aqueous solutions is to be found in hydrolytic phenomena at very high temperatures when water itself becomes much dissociated. As soon as the degree of dissociation of fused silver nitrate or chlorate has been once independently established, the above measurements will afford data for the computation of their dissociation at various other concentrations.

An attempt is being made at the present time to obtain from electrometric measurements on another type of cell the value of the dissociation constant of one of the salts used in the preceding experiments and it is hoped that shortly we may be able to state more definitely than at present whether the high conductivity of fused electrolytes is due to a great migration velocity of their ions resulting from the high temperatures to which they are subjected, or to a high degree of dissociation as has been usually assumed.

RESEARCH LABORATORY OF PHYSICAL CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY.

ENERGY NECESSARY TO IONIZE A MOLECULE BY IMPACT OF NEGATIVE IONS.

By Bergen Davis.

AS is well known, if a sufficient electrical intensity be applied to an ionized gas, all the ions produced by the external ionizing agent will be driven out and the saturation current will be obtained. If now the electrical intensity be greatly increased, the current will also be increased. Prof. J. S. Townsend[1] has shown that this increase of current is due to the production of new ions by collision of the ions already present with the neutral molecules of the gas.

An ion moving freely under a given electrical intensity will have acquired a certain kinetic energy at the end of a given path. If the kinetic energy possessed by an ion at the instant of impact is greater than the least energy necessary to bombard an electron from a molecule, ionization *may* occur.

In an early paper Townsend gives a method of calculating, from the increase of current, the least number of volts through which an ion must freely run in order to acquire sufficient energy to produce ionization by impact. The difficulty of using the method there devised, on account of a series whose terms must be separately calculated for each case, has led the writer to develop a theory that will enable one to calculate the energy of ionization directly and with considerable ease.

1. Professor Townsend gives the following theory for determining the number of new ions which one ion produces in moving one centimeter through a gas:

Assume the original ions to have a volume distribution throughout the gas. Let a force X be applied to N_0 negative ions in a gas at pressure p, and let N be the total number of ions after the N_0 ions have traversed a distance x.

[1] Townsend, Nature, Vol. LXII., August 9, 1900; Phil. Mag., Feb., 1901; Phil. Mag., June, 1902; Phil. Mag., Nov., 1903; Phil. Mag., March, 1905. Townsend & Kirkby, Phil. Mag., June, 1901.

The number of negative ions produced by N ions through a distance dx will be $\alpha N dx$, where α is the number produced by one ion in going one centimeter.

Then

$$dN = \alpha N dx N$$

and

$$N = N_0 e^{\alpha x}. \tag{1}$$

Let $n_0 l$ ions be distributed between two plates at a distance l apart, and an electrical intensity X be applied to them.

The number of ions C that arrive at the positive plate is

$$C = \int_0^l n_0 e^{\alpha x} dx = \frac{n_0}{\alpha}(e^{\alpha l} - 1)$$

and the ratio of this number to the original number is

$$\frac{C}{n_0 l} = \frac{1}{\alpha l}(e^{\alpha l} - 1).$$

If C_0 denote the original saturation current

$$C = \frac{C_0}{\alpha l}(e^{\alpha l} - 1). \tag{2}$$

By the application of this formula to experimental data Townsend has determined the values of α, in case of air, for a number of pressures and for various electrical intensities.

Some of these values of α are given in the second column of Table II. of this paper.

2. The above investigation considers the ionization to be due to impact of negative ions only. In a later paper (Phil. Mag., November, 1903), Townsend shows that the positive ions may also produce ionization by impact.

In these experiments the original n_0 ions did not have a volume distribution, but were liberated from the negative zinc electrode by the action of ultra-violet light.

By an investigation somewhat similar to the previous one he shows that.

$$\frac{n}{n_0} = \frac{(\alpha - \beta)e^{(\alpha-\beta)a}}{\alpha - \beta e^{(\alpha-\beta)a}}. \tag{3}$$

Where α is the number of ionizing impacts made by a negative ion in going a distance of one centimeter under an electrical inten-

sity X, and β is the number of ionizing impacts made by a positive ion in going the same distance under the same force.

The values of α as calculated from the experimental results in air are given in the second column of Table III. of this paper. Having thus obtained experimental values of α and the corresponding values of the electrical intensity X, a theory will be here developed that will enable one to readily calculate the least ionizing path of an ion when driven by a given electrical intensity. The ionizing path will depend upon the character of the collision between an ion and a neutral molecule. The path λ_0 determined in this investigation will be that ionizing path which an ion has when it makes normal impact with a molecule and loses all its momentum. The value of $X\lambda_0$ will then be the least number of volts through which an ion must move to produce ionization in the most favorable case.

THEORY.

Consider a gas with an ion moving through it under an electrical intensity X. Let a be the number of ionizing collisions which the ion makes in going one centimeter. If l is the mean free path of this ion, then the number of collisions of all kinds that this ion makes will be $1/l$ in going one centimeter. Let λ_0 be the least path that may produce ionization, then according to the kinetic theory of gases.[1]

$$n = \frac{1}{l} e^{-\frac{\lambda_0}{l}}$$

expresses the number of paths that are greater than λ_0. But all paths that are greater than λ_0 will not necessarily produce ionization, as the production of new ions will depend on the nature of the impact as well as the length of path. Some of the impacts will be normal to the surface of a molecule, while in many other cases the ions will strike glancing blows. The actual ionizing impacts will be

$$a = \frac{1}{l} e^{-\frac{\lambda_0 + x}{l}} (f). \qquad (4)$$

Where x is any length in addition to λ_0 which may vary from 0 to ∞, and (f) is the fraction of the paths greater than $(\lambda_0 + x)$ that result in ionization.

[1] Meyer, Kinetic Theory of Gases.

Assume a molecule to be spherical in form, and consider that ionization will take place if the kinetic energy due to the normal component of the velocity of the moving ion is equal to or exceeds the minimum energy of ionization $w = Xe\lambda_0$. The ion when it strikes the molecule must move within the cylinder $ABCD$ (see Fig. 1). If it moves along some path not in line with the center as nm for instance the kinetic energy due to the normal component of the velocity must equal or exceed $Xe\lambda_0$ in order to produce ionization. Its actual energy is $Xe(\lambda_0 + x)$ where x is a path additional to λ_0.

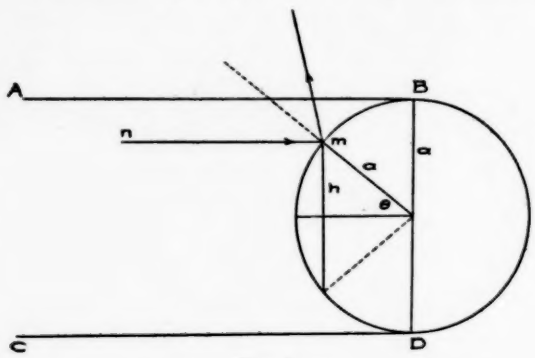

Fig. 1.

Let v be the actual velocity of the ion at end of path $(\lambda_0 + x)$, the normal component of its velocity will be

$$v_n = v \cos \theta.$$

The kinetic energy due to the normal velocity will be

$$\tfrac{1}{2}mv_n^2 = \tfrac{1}{2}mv^2 \cos^2 \theta. \tag{5}$$

But

$$\tfrac{1}{2}mv_n^2 = Xe\lambda_0$$

and

$$\tfrac{1}{2}mv^2 = Xe(\lambda_0 + x).$$

By (5)

$$Xe\lambda_0 = Xe(\lambda_0 + x) \cos^2 \theta.$$

From which

$$\sin^2 \theta = \frac{x}{\lambda_0 + x}. \tag{6}$$

The ion must strike the molecule within the cylinder $ABCD$. The probability of its striking within any angle θ, is as the ratio of

the area of base of cylinder on the segment contained in angle θ to the area of base of large cylinder. The area of base of the small cylinder is $\pi r^2 = \pi a^2 \sin^2 \theta$, and the area of base of large cylinder is πa^2. The probability of the impact occurring within the angle θ is

$$\frac{\pi a^2 \sin^2 \theta}{\pi a^2} = \sin^2 \theta.$$

This angle θ is such that when an ion has traversed a path $(\lambda_0 + x)$ its angle of impact, if it ionizes, must be equal to or less than θ.

The fraction (f) of all the impacts that produce ionization is thus equal to $\sin^2 \theta$ and equation (4) becomes

$$a = \frac{1}{l} e^{-\frac{\lambda_0 + x}{l}} \sin^2 \theta. \tag{7}$$

Introducing (6), the above becomes

$$a = \frac{1}{l} e^{-\frac{\lambda_0 + x}{l}} \frac{x}{\lambda_0 + x}. \tag{8}$$

As the ion traverses a distance dx just beyond a path $(\lambda + x)$ the number of ionizing collisions will be

$$a = \frac{1}{l} e^{-\frac{\lambda_0 + x}{l}} \frac{x}{\lambda_0 + x} \frac{dx}{l}.$$

The number of ionizing collisions which an ion makes in going one centimeter will be

$$a = \frac{1}{l} \int_0^\infty e^{-\frac{\lambda_0 + x}{l}} \frac{x}{\lambda_0 + x} \frac{dx}{l}. \tag{9}$$

This expression is not integrable in finite terms, but is given by De Haan [1] in the following form:

$$a = \frac{1}{l} e^{-\frac{\lambda_0}{l}} \left[1 + \frac{\lambda_0}{l} e^{\frac{\lambda_0}{l}} Ei \left(-\frac{\lambda_0}{l} \right) \right] \tag{10}$$

which may be written

$$al = e^{-\frac{\lambda_0}{l}} + \frac{\lambda_0}{l} Ei \left(-\frac{\lambda_0}{l} \right). \tag{11}$$

[1] Bierens de Haan, Verk. K. Akad. v-w Dl., II., blad 19.

This is the final equation which is applied to the experimental values of α as obtained by Townsend and others.

The values of the ponential integral $Ei\left(-\frac{\lambda_0}{l}\right)$ were obtained from tables by Dr. W. Láska (*Sammlung von Formeln*). The relation between αl and succeeding values of λ_0/l are given in the table below:

TABLE I.

$\frac{\lambda_0}{l}$	αl	$\frac{\lambda_0}{l}$	αl
.04	.8536	1.5	.0731
.06	.804	2	.0375
.1	.7247	3	.0106
.14	.656	4	.0032
.2	.574	5	.00099
.25	.518	6	.00032
.3	.496	7	.000142
.4	.3893	8	.000034
.6	.2762	9	.0000114
.8	.2008	10	.00000387
1	.1485		

Practical use of equation (11) can be made by plotting Table I. in a curve on a large scale with the abscissæ representing succeeding values of λ_0/l and the ordinates representing the corresponding values of αl. By means of this curve any value of λ_0/l corresponding to any given value of αl may be obtained.

The test of the validity of such a theory is that it should give a constant value of $X\lambda_0$ for all pressures and for all electrical intensities. The equation contains two unknown quantities, the mean free path l of an ion and the least ionizing path λ_0. The mean path l is a constant for any one pressure and varies inversely as the pressure. The path λ_0 depends both on the pressure and on the electrical intensity.

The third columns of Table II. are calculated by means of equation (11) from values of α obtained by Townsend (Phil. Mag., February, 1901) from experiments in which the ionization is considered as due to the impact of negative ions only.

The values of $X\lambda_0$ are as nearly constant as the nature of the experimental determinations of α could lead one to expect. The values

TABLE II.

Air.

Pressure 4.13 mm. $l = .011$ cm.		
X	a	$X\lambda_0$
200	.5	7.7
320	2.1	8.45
480	5.3	8.8
640	8.9	9.1
	Mean = 8.5	

Pressure 2 12 mm. $l = .0215$ cm.		
X	a	$X\lambda_0$
160	.9	8.6
240	2.35	8.93
400	6	9.3
560	9.5	9.46
	Mean = 9.07	

Pressure 1.1 mm. $l = .0415$ cm.		
120	1.1	9.24
160	2	9.34
320	5.5	9.5
400	8	9.54
	Mean = 9.4	

Pressure .385 mm. $l = .1184$ cm.		
120	2	9.9
200	3.4	9
320	4.5	8.96
480	5.4	8.63
	Mean = 9.12	

Pressure 171 mm. $l = .266$ cm.		
40	.65	9.45
80	1.35	9.3
160	2.2	8.25
320	2.65	9.5
	Mean = 9.12	

of l given in the above tables were those values that would make $X\lambda_0$ most nearly constant, preserving the relation that l shall vary inversely as the pressure. The mean free path of a molecule of air at room temperature and atmospheric pressure is very closely 10^{-5} cm., and 1.1 mm. pressure it is .007 cm. The value of l that satisfies equation (11) at 1.1 mm. pressure is $l = .0415$ cm. From which it is found that l is *six* times the ordinary mean free path of a molecule at the same pressure. This very large mean free path of the negative electron may be explained by two well known deductions made by Maxwell from the kinetic theory of gases: (*a*) If among molecules having distributed speeds there is one molecule that moves continuously with a speed of higher order than that of the other molecule, this molecule will have a mean free path $\sqrt{2}$ greater than the mean path of the other molecules. (*b*) If among molecules of a given size there is a particle negligibly small in comparison with the other molecules, this particle will have a mean free path *four* times that of the molecule.

It can readily be shown that the negative electron moving in the electric field here applied has a velocity at the end of its free path more than a thousand times the mean speed of a molecule. From which it immediately follows that the mean free path of an electron is $6/\sqrt{2} = 4.25$ times that of a molecule for the same velocity conditions. This ratio of paths (4.25) agrees very well with the theoretical value of *four* referred to above.

III. The values of α given in Table II. were obtained from experiments in which the ionization was considered as due to impact of negative ions only.

In a later paper (Phil. Mag., November, 1903) Townsend describes some experiments from which it is shown that the positive ions may also produce ionization by impact. The values of α as calculated by means of the corrected theory given in his later paper will necessarily be somewhat different from those in which the whole increase of current was considered to be due to the impact of negative ions only. Experimental data are given in the above paper for Air and Hydrogen. The second columns of Table III. give the values of α as obtained in air for various pressures and electrical intensities. The third columns contain the corresponding values of $X\lambda_0$ as calculated by m eansof equation (11).

TABLE III.

Air.

Pressure 2 mm. l = .0228 cm.			Pressure 1 mm. l. = 0456.		
X	α	$X\lambda_0$	X	α	$X\lambda_0$
700	10.5	11.4 volts.	350	5.25	11.4 volts.
			437	6.3	11.45 "
			525	7.27	11.49 "
Pressure .66 mm. l = 068 cm.					
350	4.8	11.55 volts.			
437	5.56	12.23 "			
525	5.9	13.6 "			

Table IV. contains similar calculations for the impact of negative electrons in hydrogen.

More recently H. E. Hurst (Phil. Mag., April, 1906) has determined the values of α for nitrogen and carbon-dioxide. I have

applied equation (11) to his values of α also. The results are given in the following tables:

In the case of air (Table III.), of hydrogen (Table IV.) and

TABLE IV.

Hydrogen.

Pressure 8 mm. $l = .01047$ cm.			Pressure 4 mm. $l = .0209$ mm.		
X	α	$X\lambda_0$	X	α	$X\lambda_0$
525	5.28	9.4 volts.	350	4.43	10.5 volts.
700	8.86	9.73 "	525	7.4	10.4 "
1050	14.8	10.5 "	700	9.6	11.7 "
Pressure 2 mm. $l = .0419$.					
262	3.7	10.5			
350	4.8	11.7			

TABLE V.

Nitrogen.

Pressure 16 mm. $l = .00285$ cm.			Pressure 8 mm. $l = .0057$.		
X	α	$X\lambda_0$	X	α	$X\lambda_0$
700	.32	10.13 volts.	350	.17	10 volts.
Pressure 4 mm. $l = .0114$.			Pressure 2 mm. $l = .0228$.		
350	1.35	10.8 volts.	350	3.54	10.5 volts.
525	3.83	11.28 "	525	7.19	11 "
700	7.08	11.4 "			
Pressure 1 mm. $l = .0456$.					
350	4.42	10.77 volts.			
525	6.41	13.1 "			

TABLE VI.

Carbon Dioxide.

Pressure 4 mm. $l = .0117$ cm.			Pressure 2 mm. $l = .0234$.		
X	α	$X\lambda_0$	X	α	$X\lambda_0$
350	2.47	9.1 volts.	700	11.3	10.5 volts.
700	9.28	9.9 "	1,400	21.21	9 "
Pressure 1 mm. $l = .0468$.			Pressure .5 mm. $l = .0936$.		
700	10.68	8.8 volts.	525	6.41	9.8 volts.
875	11.83	8.9 "	700	6.74	10.3 "
1,050	12.68	11.1 "	875	7.5	9.3 "

nitrogen (Table V.), the only values of l that would make $X\lambda_0$ nearly constant for the various pressures and electrical intensities were l equal to $6/\sqrt{2}$ times the mean free path of a molecule for any pressure and the same conditions of velocity. In the case of carbon dioxide (Table VI.) the only values of l that would make $X\lambda_0$ constant were l equal to $9/\sqrt{2}$ times the mean free path of a molecule for the same velocity.

CONCLUSION.

The values of $X\lambda_0$ given in Table II. although nearly constant among themselves differ somewhat from those values for air given in Table III.

This disagreement is to be expected, since the values of α for air given in Table II. were obtained by means of a theory that neglected the ionization due to the impact of positive ions. In Table III. the ionization due to the impact of positive ions is allowed for and the values of α there given are probably more nearly the true values for those pressures and electrical intensities.

The mean results obtained are given in the table below:

Gas.	R	$X\lambda_0$	$X\lambda_0 e$
Air.	4.25	11.8 volts.	1.22×10^{-11} ergs.
Nitrogen.	4.25	11 "	1.14×10^{-11}
Hydrogen.	4.25	10.55 "	1.09×10^{-11}
CO_2.	6.38	9.67 "	1.0×10^{-11}

The charge e is here taken as 3.1×10^{-10} E.S. (H. A. Wilson). R is the ratio of the mean free path of an electron to that of a molecule for the same velocity conditions.

PHŒNIX PHYSICAL LABORATORY, COLUMBIA UNIVERSITY,
October 27, 1906.

THREE-COLOR INTERFERENCE PICTURES.

By Herbert E. Ives.

(Preliminary Paper.)

THE subject of the following paper is an application of the Lippmann process to the production of three-color pictures. The method consists in using a set of three-color negatives to make a picture composed of juxtaposed colored lines, red, green and blue, after the manner of the Joly color picture, substituting, however, the laminated structure of the Lippmann film for the pigments which impart color to the true Joly picture. By this combination of the three-color and standing-wave processes pictures are obtained by an indirect though wholly photographic means, possessing the fidelity of the best three-color processes with advantages peculiar to the Lippmann picture. The colors are in the picture itself, so that no viewing device is necessary to render them visible, and from the original three-color negatives an indefinite number of color pictures can be made.

Up to the present Lippmann photographs of natural objects (as distinguished from spectra or monochromatic sources) have been made directly in the camera. A departure from this simple and straightforward procedure of course needs ample justification. This will be found in a consideration of previous attempts to photograph mixed colors, such as those of natural objects, and the conclusions, both theoretical, and practical, to be drawn therefrom.

It has long been recognized that while spectra are easily and satisfactorily photographed by the Lippmann process, such objects as landscapes, still life, etc., are very difficult and rarely reproduce with great fidelity. The principal reasons therefore may be briefly summarized as follows:

1. Complete isochromatism of plates is essential.

In photographing spectra with non-isochromatic plates all the colors may be made to give strong action by mere long exposure.

Additional exposure of the photographically more active colors after their maximum effect is produced causes no increase of action within wide limits. In photographing natural objects recourse to long exposure to produce isochromatic action is obviously destructive of light and shade values, since these are rendered entirely by difference of exposure. The dependence of the best results on careful choosing of exposure has often been noticed.[1]

2. To obtain a close approximation to the color of the object photographed the lamina system must be of considerable depth and must be transparent. Neither of these conditions is fulfilled. The Lippmann film is very thin (not over .01 mm.) and strongly absorbing.

3. It appears from the microsections made by H. Lehmann[2] that the lamina system, owing to the scattering of the incident light and other causes, dies down much more rapidly than that predicted from calculation. The light reflected is therefore always less pure than that acting to produce the laminæ. The frequent resemblance of Lippmann pictures to tinted Ambrotypes and Daguerrotypes may be explained by this general admixture of white.

4. From experiments made by H. Lehmann[3] on photographing two and three colors simultaneously it appears (and theoretical study of the lamina system resulting from mixed colors confirms) that mixed colors are rendered with a loss of luminosity of the components as compared with the rendering of the components alone.

It follows from this that if colors of different degrees of purity occur in an object photographed their reflective luminosities will be wrongly rendered. For instance, an area illuminated by a sodium flame and an area illuminated by a broad spectral region including red and green, while appearing the same color to the eye, and adjusted to be the same apparent brilliancy, would be rendered as of quite different brilliancies. Certain types of colors, such as those of some aniline dyes, in whose spectra two or more maxima occur, would suffer greatly in this respect.

[1] R. Neuhaus, Die Farbenphotographie nach Lippmanns Verfahren, 1898, p. 45. "Das Bild giebt nur dann die Farben richtig wieder, wenn die Belichtungszeit richtig getroffen wurde. Halbfach Über- odor Unterexposition genugt schon vollständig die Platte zu verderben."

[2] "Beiträge zur Theorie und Praxis der directen Farbenphotographie," 1906, p. 81.

[3] L. c., p. 14.

All of these facts impose obstacles to the complete success of the original Lippmann process. A detailed study of the rendering of mixed colors and the conditions essential for the best results is now being carried on by the writer and will be published in the near future. The above conclusions on the reproduction of colors of all types, have, however, been confirmed and the recourse to the three color process as the means of rendering all kinds of colors faithfully (to the eye), while employing the Lippmann film, is the practical result.

The determining reason for this step is as follows: The Lippmann process is, as seen above, not fitted to render all types of colors faithfully. For the three-color process all that is needed are narrow spectrum bands; these the Lippmann film is thick enough and transparent enough to give.

Proceeding now to the practical details as worked out. It is, of course, necessary to have a set of three-color negatives or color records. Each of these must represent the amount of one of the primary colors, red, green, and blue, necessary to mix with the proper amounts of the others to counterfeit to the eye the color of the object photographed. The three-color records used were positives made for the Krōmskōp.[1]

The first apparatus constructed consisted of an enlarging camera by means of which an image of any one of the three-color positives was projected on the plate; a heliostat to send a beam of sunlight through positive and projecting lens, and an opaque line screen or grating, in contact with the plate, having opaque spaces twice the width of the transparent. By means of this latter one third of the surface of the plate could be exposed at a time. For colored light three color-screens, identical with those used in the Krōmskōp were tried; a ruby-red glass, a pot-green glass, and a combined cobalt-blue and signal-green glass. These give narrow, well separated spectrum

[1] The Krōmskōp system is based on Maxwell's color mixture diagram. The three negatives are made through color screens which with the plates used give intensity curves that correspond to the Maxwell color curves representing the three primary sensations. Those curves give the amounts of three narrow spectrum bands (near *C*, between *E* and *F*, between *F* and *G*) to mix to reproduce to the eye both the color and luminosity values of all parts of the solar spectrum. The application of Maxwell's analysis to three-color photography was first published by F. E. Ives in 1888.

bands, quite pure enough to give the best results. The procedure was to make three exposures in succession, between each of which the three-color positive was changed, the color screen changed, and the opaque-line screen moved the width of a transparent space (one three-hundredth of an inch). The method is in all respects similar to that employed by the writer to produce diffraction color pictures.[1]

It was soon found that much purer colors must be used than those furnished by the color screens, for this reason: The spectrum band by which the plate was illuminated, reproduced, as examination of the photograph in the spectroscope showed, as a much wider one. The triple-line pictures, therefore, instead of showing in the spectroscope three isolated bright bands gave a continuous spectrum with slightly shaded spaces in the yellow and blue-green. This was confirmed by exposures with spectrum bands of varying width from a monochromatic illuminator. In all cases it was found on spectroscopic examination that these bands were rendered by broad, not sharply defined ones of from five to ten times the width of the original. The most monochromatic source then at hand, a sodium flame, was photographed, and the plate showed in the spectroscope a fairly narrow band, although some red and green light was still visible. Colors as pure as that obtained in this way would be quite satisfactory for three-color work. Suitable red, green and blue line sources were not at the time available, so, as the best that could be done, portions of the spectrum of about eighty A.U. width from a monochromatic illuminator were tried. The colored light was thrown on the three color positive, which was placed directly in front of the opaque-line screen and the plate, and so cast a shadow.

With this apparatus three-color standing-wave pictures were obtained which compare favorably with the Krōmskōp and have qualities rarely, if ever, seen in the ordinary Lippmann pictures. The color and luminosity values are faithfully rendered and the peculiar metallic appearance so common in most interference pictures is entirely absent. They are not, of course, color pictures taken directly in the camera, the ideal for which we aim, but they are faithful color pictures produced by entirely photographic means; they are held in

[1] PHYSICAL REVIEW, June, 1906, p. 339.

the hand to observe, and may be duplicated indefinitely. They do not fulfill the popular conception of a color photograph so well as would Lippmann pictures taken directly in the camera, were the latter free from the unavoidable defects outlined above. They are perhaps the nearest we can come to a true color photograph at present.

The defects of these new three-color interference pictures so far made are due to the inadequate means at hand when the work was done. The colored light used was not as monochromatic as was desired. The three bright strips of color seen when one examines the photographs with the spectroscope are as a consequence rather wide and the spaces between not quite black, hence some degradation of color values results. It is intended as soon as possible to make pictures by means of monochromatic light furnished by sources such as the cadium lines, and to make the triple (Joly) lines at least two hundred to the inch, so that they become practically invisible.

With these improvements the pictures should rank as one of the most perfect applications of the three-color process.

The plates used were prepared according to the formula published by Valenta[1] with the exception that it was found necessary to double the quantity of gelatin; this may, however, have been due to the kind of gelatin used.[2] The pictures were mounted under a prism according to the usual method. To destroy all extra reflections possible the back of the glass and the lower surface of the prism were ground with emery before the application of asphaltum varnish to the one and Canada balsam to the other. It was further found advantageous to substitute gum styrax ($n = 1.58$) for Canada balsam in mounting the prism. By this the surface reflection from the film is less than with the balsam, and in addition (if the lower side of the prism is ground) a slight diffusion of light results so that the picture is visible through a wider angle, and the reflected image of the source of light (such as a gas flame) no longer well enough defined to be disturbing.

PHYSICAL LABORATORY, JOHNS HOPKINS UNIVERSITY,
October 7, 1906.

[1] Die Photographie in natürlichen Farben, 1894, p. 52.
[2] "Gold Label," sold by Eimer & Amend, New York.

THE ABSORPTION OF ALPHA RAYS IN GASES AND VAPORS.

BY E. P. ADAMS.

AT a meeting of the Physical Society held in December, 1905,[1] the writer described some experiments made to determine the maximum distance between a source of alpha rays and a zinc sulphide screen at which the well-known scintillations could be seen. The results arrived at were that this maximum distance was inversely proportional to the pressure of the gas, the temperature remaining the same; and that in different gases the product of the pressure and maximum distance was inversely proportional to the sum of the square roots of the weights of the atoms contained in the molecules of the gas. The latter result is similar to that obtained by Bragg and Kleeman[2] for the so-called "stopping-power" of various gases, vapors, and metals for the alpha rays from radium, the electrical method of measuring the ionization produced by the rays being employed. According to their experiments, the absorption of alpha rays by various substances is not an absorption of the rays in the ordinary sense, but an absorption of a portion of their energy which is spent in ionization, as a result of which the velocity of the alpha rays is continually diminished. When their velocity falls below a certain limiting value the alpha rays lose their ionizing property. These results have been confirmed and extended by Rutherford,[3] who measured the velocity of the alpha particles after having passed through various numbers of layers of aluminium foil. Rutherford also showed that the photographic and phosphorescent effects produced by the alpha rays ceased with their ionizing effects.

The delay in publishing the complete results of these experiments is due to a desire to include the results for the monatomic gases

[1] PHYSICAL REVIEW, February, 1906, p. 111.
[2] Phil. Mag., 10, p. 318, 1905.
[3] Phil. Mag., 10, p. 163, 1905.

argon and helium which were thought to be of special interest in view of the relation which was found to hold for the different gases and vapors tried.

The source of the alpha rays in these experiments was polonium, which is specially suitable as it does not emit any beta-rays. The polonium was separated from the mineral carnotite. As this mineral is comparatively easy to obtain in this country it may be of interest to describe the method of preparing the polonium, the process being very simple. Carnotite, which occurs disseminated through sandstone, is easily soluble in hydrochloric acid. The excess of acid is driven off by heat, water added, and hydrogen sulphide passed into the solution. The precipitate is filtered, thoroughly washed with water, and dissolved in nitric acid. The sulphur which separates is removed by filtration. This nitric acid solution contains the polonium, along with bismuth, lead, copper, etc. It is advisable to add to this solution a small quantity of bismuth, as the polonium is precipitated with the bismuth, and it is desirable to have a rather larger quantity of bismuth precipitated than that originally contained in the carnotite. The nitric acid solution is then evaporated nearly to dryness to remove the excess of free acid, and a large quantity of water added. This precipitates bismuth hydroxide, and with it, the polonium. After filtering this precipitate, it is dissolved in the smallest possible quantity of hydrochloric acid. This last solution contains all the polonium. By placing a polished bismuth plate in this solution, in the course of a few days the polonium is nearly all deposited upon its surface. There is thus obtained, from a pound or two of carnotite, a layer of polonium upon the bismuth plate which is sufficiently active for experiments of this kind.

A description of the apparatus used in these measurements follows: The active bismuth plate, *A*, was carried at the end of a glass rod which floated on a column of mercury whose height could be regulated by raising or lowering a mercury reservoir, *D*. The measuring tube, *F*, which was made of glass, was closed at the top by a glass plate, *B*, on the under side of which the phosphorescent zinc sulphide was cemented. The tube could be exhausted by means of a mercury pump, and the various gases admitted, the

pressure being given by a mercury gauge, *E*. The zinc sulphide, in the earlier experiments, was held to the glass plate by a very small amount of Canada balsam; with certain of the vapors used it was found that the Canada balsam was attacked, and water-glass was then used as a cement which proved to be entirely satisfactory. The glass plate was ground to fit accurately the top of the measuring tube; a small amount of water-glass then made the tube perfectly air-tight. The zinc sulphide screen was viewed through a magnifying glass, *C*.

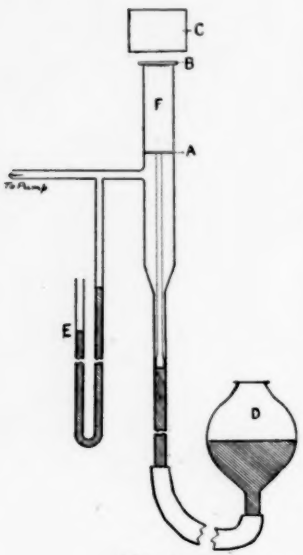

Fig. 1.

The object of the experiment was to measure the maximum distance between the active plate and the zinc sulphide screen at which the scintillations could be seen through the magnifying glass. For this purpose the mercury reservoir was raised or lowered until the scintillations just appeared or just disappeared. A number of settings were thus made at each pressure and the average taken as the proper maximum distance corresponding to that particular pressure. For distances less than about 10 cm. it was found that the disappearance or appearance of the scintillations was very sharp so that the successive settings were in very close agreement with each other. For greater distances, owing mainly to the spreading out of the alpha rays, the number of scintillations seen was much smaller and the successive settings were not in so close agreement. It was frequently observed that scintillations appeared when the polonium was at too great a distance for the alpha rays to produce them, and even when the polonium was taken out from the tube. These scintillations were of a different character than those due to the alpha rays; they appeared to be much brighter. It is probable that these were due to changes in the cementing material, partly temperature changes, and the drying out of the cement which caused a sudden pressure to be exerted upon the zinc sulphide, thus causing light effects. It is known that phosphorescent zinc

sulphide is extremely sensitive to mechanical shocks. These scintillations produced no confusion as with a little practice they could easily be distinguished from the scintillations due to the alpha rays. A similar spontaneous scintillation of zinc sulphide has been observed by Schenck and Mihr.[1]

In preparing the gases used only the ordinary precautions were taken to have them pure. They were dried by means of phosphorus pentoxide except in the case of acetone, which was decomposed by the phosphorus pentoxide. The liquids whose vapors were examined were, with one exception, the ordinary "chemically pure" products of commerce. Nickel carbonyl was prepared by the method of Mond, Langer and Quincke.[2] Argon was obtained by passing air over heated copper and magnesium twice, by means of which the oxygen and a large part of the nitrogen was removed. The remaining nitrogen was removed by passing an electric arc between platinum terminals through the gas collected over a solution of caustic potash with the repeated addition of oxygen. Finally the remaining oxygen was removed by means of solid phosphorus. Helium was obtained by heating the mineral fergusonite in a vacuum. This mineral, which came from Llano Co., Texas, gave off, by the application of heat alone, about 0.1 c.c. of helium per gram. The resulting gas was freed from nitrogen and other impurities by means of an electric arc in the same manner as employed for argon. It was necessary to add the oxygen in very small quantities at the beginning as hydrogen is given off by heating this mineral, due to a reduction process, and with too much oxygen present a serious explosion might result on starting the arc. When the helium so prepared was put into the testing tube it was found that the scintillations could not be made to disappear even by removing the polonium altogether. This was due to the fact that fergusonite contains a certain amount of radium, and on heating it the radium emanation was collected along with the helium. It was therefore necessary to wait several months until the emanation had disintegrated sufficiently to allow measurements to be made in the regular way. By means of liquid air it would have been possible to freeze the emanation out of the helium at once.

[1] Ber. deut. chem. Ges., 37, p. 3464, 1904.
[2] Trans. Chem. Soc. London, 57, p. 749, 1890.

The vapors were introduced into the testing tube as follows. A flask provided with a tap funnel was sealed on to the apparatus and the whole exhausted. A small amount of the liquid could then be introduced into the flask without admitting any air. By measuring the pressure, and knowing the tension of the saturated vapor, an estimate could be formed as to the purity of the vapor.

Observations were always made at night in the dark as then the eye is much more sensitive to effects of this kind than in the daytime. It was found that after thirty to forty minutes of observation the eye became too tired and it became very difficult to get concordant results.

The following tables are characteristic of the results obtained. In each table the first column gives the pressure, p, the second the maximum distance between the polonium and the zinc sulphide screen, d, and the third the product, pd; d is measured in centimeters, and p in centimeters of mercury.

Air.			Ethyl Iodide.		
p	d	pd	p	d	pd
75.54	3.49	264	9.60	8.74	83.9
69.69	4.20	293	8.65	9.43	81.6
52.86	5.03	266	7.65	10.67	81.6
22.14	12.53	277	7.20	11.33	81.6
15.79	17.72	280			
		Average, 276			Average, 82.2

Oxygen.			Nickel Carbonyl.		
p	d	pd	p	d	pd
70.15	4.03	283	22.8	2.38	54.3
59.30	4.70	279	21.0	2.53	53.1
44.15	6.09	269	17.9	2.97	53.2
34.07	7.87	268	16.6	3.53	58.6
18.60	14.33	267	14.1	4.29	60.5
15.60	16.06	251	9.5	5.97	59.4
			6.4	8.58	54.9
			4.5	11.58	52.1
		Average, 269			Average, 55.8

From these tables it is seen that the product, pd, is approximately constant for any one substance. The deviations appear to be within

the limits of experimental error. A slight tendency has been noticed for this product, for many substances, to decrease with the pressure, but it seems probable that this is caused by the decreased sensitiveness when the distance between the polonium and the zinc sulphide screen becomes large.

The complete results for all the substances examined are given in the following table. The first column of figures gives the sum of the square roots of the atomic weights of the atoms in the molecules. Thus for carbon dioxide we have:

$$\Sigma\sqrt{A} = \sqrt{C} + 2\sqrt{O} = \sqrt{12} + 2\sqrt{16} = 11.5.$$

For air:

$$\Sigma\sqrt{A} = \frac{4 \times 2\sqrt{N} + 2\sqrt{O}}{5} = \frac{4 \times 2\sqrt{14} + 2\sqrt{16}}{5} = 7.6.$$

The second column of figures gives the average value of the product, pd, for several different pressures found by experiment; and the last column gives the product of the two preceding ones.

		$\Sigma\sqrt{A}$	pd	$pd\Sigma\sqrt{A}$
Hydrogen,	H_2	2.0	1,108	2,216
Helium,	He	2.0	954	1,908
Argon,	A	6.32	301	1,902
Methane,	CH_4	7.46	292	2,178
Air,		7.60	276	2,098
Oxygen,	O_2	8.00	269	2,152
Carbon dioxide,	CO_2	11.46	186	2,132
Cyanogen,	C_2N_2	14.42	153	2,206
Carbon bisulphide,	CS_2	14.78	125	1,848
Methyl iodide,	CH_3I	17.73	110	1,950
Acetone,	C_3H_6O	20.38	107	2,181
Ethyl bromide,	C_2H_5Br	20.86	98	2,044
Chloroform,	$CHCl_3$	22.31	88	1,963
Ethyl iodide,	C_2H_5I	23.19	80	1,855
Carbon tetrachloride,	CCl_4	27.26	78	2,126
Ether,	$C_4H_{10}O$	27.84	88	2,450
Pentane,	C_5H_{12}	29.30	77	2,256
Nickel carbonyl,	NiC_4O_4	37.50	56	2,100
				Average, 2,081

It is thus seen that the product of the pressure, the maximum distance at which the scintillations can be seen, and the sum of the

square roots of the atomic weights is very nearly constant over a wide range. The largest deviation is in the case of ether.

The fact that the absorption of complex molecules for the alpha rays can be expressed as a sum of terms depending only on the atoms in the molecules indicates that the effective collisions of the alpha rays are not with the molecules as a whole but with the atoms in the molecules. The experimental facts can be explained by assuming that the number of collisions that each alpha particle makes is proportional to the total number of atoms present in the gas through which it passes, and that at each collision the alpha particle loses an amount of its energy proportional to the square root of the weight of the atom it collides with. But the reason for the square root is difficult to see. Bragg and Kleeman suggested that the atoms have a disk-like form; assuming then that ions can be formed only on the circumference of the atom, the circumference being proportional to the square root of the whole, the square root law would seem to be explained. But this seems a very artificial hypothesis; and moreover, we have no evidence that the atoms have a disk-like form. There is some evidence from the kinetic theory of gases that the cross-section of the molecule is equal to the sum of the cross-sections of the constituent atoms, and hence that the molecules have a disk-like form. But this has no bearing on the present problem as it is evident that molecular structure does not enter into it. In a more recent paper[1] Professor Bragg has again suggested this same explanation, with the extension that some effect is produced on an alpha particle when it strikes the center of an atomic disk. Therefore the stopping power of an atom for an alpha particle should be proportional to

$$a\sqrt{w} + bw$$

where a and b are constants, b being small compared to a, and w is the weight of the atom. The scintillation method is not accurate enough, however, to make it worth while attempting to confirm this expression.

PRINCETON UNIVERSITY,
PRINCETON, N. J.

[1] Phil. Mag., May, 1906, p 617.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

MINUTES OF THE THIRTY-FOURTH MEETING.

A REGULAR meeting of the Physical Society was held in the Kent Chemical Laboratory of the University of Chicago on Saturday December 1, 1906. Past President A. A. Michelson presiding.

The following papers were presented:

1. Spark Discharges in Gases and Vapors. JOHN E. ALMY, University of Nebraska.

2. On the Magnetic Behavior of Certain Alloys of Nickel. BRUCE V. HILL, University of Kansas.

3. An Experimental Gyroscope for Quantitative Work. FREDERICK E. KESTER, Ohio State University.

4. Upon the Discharge of Electrons from Ordinary Metals Under the Influence of Ultra-violet light. R. A. MILLIKAN and GEORGE WINCHESTER, University of Chicago.

5. An Inanimate Demon. A. B. PORTER, Chicago.

6. On Multiple Crossed Gratings. A. B. PORTER, Chicago.

7. On the Ruling of Diffraction Gratings. A. A. MICHELSON, University of Chicago.

8. The Effect of Temperature on Metallic Spectra. H. G. GALE, University of Chicago.

9. The Radiation Constants and Temperature of the Nernst Glower. C. E. MENDENHALL and L. R. INGERSOLL, University of Wisconsin.

10. Standard Cells. K. E. GUTHE and C. L. VON ENDE, University of Iowa.

11. Heat of Dilution. F. L. BISHOP, Bradley Polytechnic Institute.

12. The Viscosity of Water at Low Rates of Shear. LAWRENCE E. GURNEY, University of Idaho. Introduced by A. A. Michelson.

13. The Bridge Method for Comparison of Condensers. FREDERICK E. KESTER, Ohio State University.

14. A Method for the Determination of Electrolytic Resistance and Capacity. A. H. TAYLOR, University of Wisconsin.

15. On the Effects of the Electrical Discharge on the Acetylene Flame. C. F. LORENZ, Johns Hopkins University.

16. Change of Phase Due to the Passage of Electric Waves Through Thin Films and the Index of Refraction of Water for Such Waves. Wm. R. BLAIR, University of Chicago.

17. The Temperature of the Moon. WM. W. COBLENTZ, Bureau of Standards, Washington.

18. The Temperature of the Moon. FRANK W. VERY.

19. Note on the Fluorescence of Sodium Vapor. ERNEST MERRITT.

20. The Relation between Uranium and Radium. H. N. McCOY and W. H. ROSS.

21. Note on the Behavior of Small Particles on the Nernst Glower. C. E. MENDENHALL and L. R. INGERSOLL.

A resolution was adopted directing the attention of the Council to the desirability of holding a regular yearly meeting in Chicago.

ERNEST MERRITT,
Secretary.

UPON THE DISCHARGE OF ELECTRONS FROM ORDINARY METALS UNDER THE INFLUENCE OF ULTRA-VIOLET LIGHT.[1]

BY R. A. MILLIKAN AND GEORGE WINCHESTER.

THIS investigation was undertaken (1) to determine whether or not the discharge of negative electricity which takes place from metals illuminated by ultra-violet light is a function of the temperature when all secondary temperature effects due to the surrounding medium are eliminated by placing the metals in a very high vacuum; (2) to determine the order in which the common metals arrange themselves in relation to their power of emitting electrons under the influence of a given source of ultra-violet light: (3) to determine the relative velocities of projection of electrons from the various metals by measuring the positive potentials acquired by them under the influence of ultraviolet light; (4) to determine whether this velocity is a function of the temperature.

The results of the investigation may be summarized as follows:

I. Within the limits of observational error, which amount to but one or two per cent., the photo-electric effect, like radio-activity is wholly independent of temperature for all of the metals experimented upon, namely, copper, gold, nickel, brass, silver, iron, aluminium, magnesium, antimony, zinc and lead.

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society, December 1, 1906.

II. The relative rates of discharge of electrons from the above metals, under identical conditions, were as follows:

Metal.	Discharge Rate in Scale Divisions.	Melting Point.
Copper.	25.10	1050° C.
Gold.	24.70	1050 "
Nickel.	24.00	1450 "
Brass.	23.80	——
Silver.	17.16	968 "
Iron.	16.40	1350 "
Aluminium.	14.90	625 "
Magnesium.	11.00	750 "
Antimony.	4.00	632 "
Zinc.	1.20	433 "
Lead.	.90	326 "

This order is not at all in accord with that found in the Volta contact series as previous experiments had indicated might be the case, nor does it agree entirely with the order in which the above metals exhibit any familiar physical property. Its closest relationship seems to be to that of the melting point series which is given the last column in order to facilitate comparison.

III. The positive potentials in volts acquired under identical conditions by the metals experimented upon are given in the following table. If the discharge takes place into a perfect vacuum the maximum velocity of projection of the electrons may be calculated from the formula $v = \sqrt{2e/m \times P}$, in which P is the positive potential acquired and e/m is 1.1×10^7.

Metal.	Potential in Volts.
Silver.	1.34
Iron.	1.22
Gold.	1.21
Brass.	1.17
Copper.	1.13
Nickel.	1.12
Magnesium.	.839
Aluminium.	.738
Antimony.	.39
Zinc.	.19
Lead.	.0

The order in which the metals occur in this table is wholly different from that of the preceding table and apparently has no connection either with the atomic weights of the elements or with any other of their known properties.

IV. The potentials acquired were found to be in all cases wholly independent of temperature — a fact which appears to warrant the conclusion that the kinetic energy of an electron within the atom of which it forms a part is not influenced by temperature changes.

THE EFFECT OF TEMPERATURE ON METALLIC SPECTRA.[1]

BY H. G. GALE.

THIS investigation was undertaken in the hope of finding in the laboratory some method of differentiating the spectral lines of Ti, Va, Cr, Mn and Fe which are affected in sun spots. The work was done in the laboratory of the solar observatory on Mt. Wilson, in collaboration with Mr. Hale and Mr. Adams, and was in the nature of a sequel to the important work which had been done by them on the spectra of sun spots.

It was found that when the arc spectrum of one of the elements named was taken with a two ampere current and compared with a spectrum taken on the same plate with a 25 or 30 ampere current, certain lines were strengthened and a few weakened as compared with the rest of the spectrum. Further examination showed that the lines which were strengthened in the two ampere current were in practically all cases, lines which are strengthened in sun spots, and that the lines which are weakened in sun spots are the lines which were weakened in the two ampere arc.

It was found further that in practically all cases lines which were weakened in the two ampere arc as compared with the 30 ampere arc are lines which are enhanced in the spark relatively to the arc.

Of 220 spot lines examined 204 were definitely strengthened in the weak arc and the remaining 16 lines were either unchanged or changed so slightly as to be uncertain.

Of 32 lines weakened in spots 29 were clearly enhanced and 3 were unchanged in the spark. Of these 32 lines 24 were clearly weakened, 7 were not seen and I showed no change in the two ampere arc.

Extending the investigation into the violet beyond the region which is apparently affected in sun spots, of 109 lines enhanced in the spark 84 were weakened, 20 not seen and 5 were unaffected in the weak arc.

Of 152 prominent solar lines which are not affected in spots none showed strengthening in the weak arc, 133 were unchanged and 19 doubtful, possibly slightly weakened.

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society, December 1, 1906.

The only directly contradictory evidence found was in the case of the two iron lines at λ 5429.91 and λ 5447.13. Both appear to be enhanced in the spark, although they are strengthened in both the weak arc and in spots.

The cause of the variation between the spectra of the 2 ampere and 30 ampere arcs which naturally suggested itself was that the 2 ampere arc was cooler than the other. To test this hypothesis spectra were photographed from the outer portions of the flame coming from a 30 ampere arc and compared with spectra from the middle of the core, between the poles. The agreement between the weak arc and flame was entirely satisfactory, the great majority of the lines being affected not only in the same direction but by the same amounts.

To further test the effect of temperature as distinguished from any possible electrical effect Fe, Mn and Cr were in turn vaporized in an electric furnace and the spectra photographed. All of the lines in the region examined were affected in the same direction as in the two ampere arc and by practically the same amounts.

It seems permissible therefore to conclude that the spark spectrum corresponds to a higher temperature than the arc spectrum, that the variations between the 30 ampere spectrum and that from the weak arc, flame or furnace are due to the lower temperature of the latter and that the differences between sun and spot spectra are due to the same cause.

Mr. Adams has recently found that the spectrum of Arcturus is in remarkable agreement with that of sun spots, and Mr. Hale and Mr. Adams have found that the spectrum of α Orionis shows still greater variations in the same direction. It seems probable therefore that the Sun, Arcturus and α Orionis are in order of descending temperature.

It does not follow that temperature differences offer the only means of producing changes in the relative intensity of the lines in the metallic spectra, but variations in temperature appear to afford a simple and satisfactory explanation of the changes in the relative intensity of the so-called "spot lines" as observed in the laboratory, in sun spots and in stars.

RYERSON PHYSICAL LABORATORY,
November 9, 1906.

STANDARD CELLS.[1]

BY K. E. GUTHE AND C. L. VON ENDE.

WE constructed some standard cells with electrolytic mercurous sulfate, prepared by us, and with sulfate received from Dr. Hulett. The agreement between the electromotive forces for cells of the same series is within 2 in 100,000. Slight variations in the method of con-

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society, December 1, 1906.

struction were made and their influence upon the electromotive force determined.

Comparison of these new cells with those used last year for the absolute determinations, showed that the Clark cells agreed with the old, but that the cadmium cells had a considerably higher electromotive force than the old, the changes of which have been quite irregular.

While the initial electromotive force of the new cadmium cells agrees very closely with the value found by Hulett for freshly set up cells, it decreases rapidly in a few weeks and has now a value 0.0001 volt lower than at first.

Mercury distilled twice in an ordinary vacuum still gives the same results as mercury distilled by Hulett's method. No difference was noticed between amalgam prepared in the usual way and electrolytic amalgam. Clear and cloudy cadmium sulfate crystals produce no difference in the electromotive force of the cadmium cells.

Clark cells with electrolytic, coarsely grained mercurous sulfate have immediately after construction an electromotive force of 1.4204 volts at 25° C., within a few hundred thousandths of a volt and remain constant in course of time.

Cadmium cells with practically identical electrical behavior cannot be constructed at the present time by different observers.

THE BRIDGE METHOD FOR COMPARISON OF CONDENSERS.[1]

BY FREDERICK E. KESTER.

THEORETICAL considerations show that the two possible arrangements of galvanometer and battery, in the bridge network for the comparison of condensers, give different values for the quantities of electricity which flow through the galvanometer when the conditions of exact balance are disturbed by equal changes in the value of one of the balancing resistances. With the galvanometer connected between the junction of the two condensers and the junction of the two resistances, the expression for the quantity flowing through the galvanometer is

$$\int_0^\infty i \cdot dt = C_2 \cdot E \cdot \frac{\Delta R_2}{R_1 + R_2}.$$

The other connection, with the galvanometer and battery interchanged gives

$$\int_0^\infty i \cdot dt = C_2 \cdot E \cdot \frac{\Delta R_2}{R_1 + R_2 + G}.$$

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society, December 1, 1906.

With galvanometers of high resistance the difference between the values of these two expressions is considerable.

Experimental results obtained with various condensers and various values of the balancing resistances verify these formulæ within the limits of observation errors. The verification may be shown by comparison of the product of $(R_1 + R_2)$ and the galvanometer deflection per ohm change in R_2 in the first case, with the product of $(R_1 + R_2 + G)$ and the galvanometer deflection per ohm change in R_2 in the second. The products should be equal since the galvanometer deflections are proportional to $\int i \cdot dt$ if a ballistic instrument be used. In the experimental work for the results given below the same value of E was used throughout, the same galvanometer conditions were maintained and the same condenser was used always as C_2; the products given in the last column of the tables should, therefore, be approximately equal.

GALVANOMETER RESISTANCE 1,916 OHMS.

Condensers: C_1, Elliott Bros., ⅓ m. f., No. 848; C_2, Elliott Bros., ⅓ m. f., No. 847.

Connection.	R_1	R_2	Defl. per Ohm.	Product.
I.	2,000	1,980	0.064_7	258
I.	200	198	0.63_7	254
II.	2,000	1,980	0.039_4	232
II.	200	198	0.10_9	252

Condensers: C_1, Elliott Bros., 1 m. f., No. 56; C_2, Elliott Bros., ⅓ m. f., No. 847.

Connection.	R_1	R_2	Defl. per Ohm.	Product.
I.	2,000	6,224	0.031_5	259
I.	200	622	0.32_8	270
II.	2,000	6,224	0.025_7	261
II.	200	622	0.09_8	268

THE TEMPERATURE OF THE MOON.[1]

BY W. W. COBLENTZ.

AT the Ithaca meeting of the society, June, 1906, the writer offered as a side issue to his main work on reflection spectra, some deductions relating to the temperature of the moon, which subsequent consideration has led him to believe erroneous. At that time the experimental

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society, December 1, 1906.

work of Very[1] and the calculations of Poynting[2] were unknown to him, and the conclusions were based upon the original curves published by Langley.

The work of these two investigators is quite convincing that the temperature of the lunar surface must rise to at least 300° abs., and the problem is reduced to the calculation of the relative intensities of the energy emitted and reflected by the moon at 8 to 10 μ. This has been done and the results show that the radiation from the sun which the moon reflects to the earth is only from $\frac{1}{4}$ to $\frac{1}{16}$ the energy which the moon radiates to us, assuming the temperature to be 300° abs.

The writer regrets the fact that the former deductions have gotten into print, for they accentuate the not infrequent occurrence of similar cases where writers have published conclusions before the subject has been thoroughly considered. A fuller discussion of this subject is now in press along side with the work on reflection spectra.

Note on the Temperature of the Moon.[3]

By Frank W. Very.

THE supposition that the Moon may reflect specularly a portion of the Sun's rays between 8.5 and 10 μ is rendered probable from Professor E. F. Nichols' discovery that quartz has bands of metallic reflection in this region, and from the recent announcement by Dr. W. W. Coblentz that various common silicates possess similar properties.

But this specular reflection has never been observed, and must not be confounded with the maximum in the lunar spectrum of about the same wave-length, since the latter belongs to a continuous spectrum and not to a band. Moreover, the maximum heat in the lunar image is found, not at the position where specular reflection would place it, but near the point of maximum insolation. Consequently, the observed maximum in the extreme infra-red spectrum of the Moon is due to the proper radiation from the heated lunar surface.

During totality of a lunar eclipse of the darker sort, the amount of sunlight refracted into the shadow by the Earth's atmosphere, and reflected from the Moon, becomes vanishingly small; but the true infra-red radiation of the Moon may still be as much as one per cent. of its value before the eclipse, and the heat is promptly restored, or very nearly restored, after the eclipse is over, showing that, although a thin super-

[1] Astrophys. Jour., 8, p. 199, 1898.

[2] Jahrbuch der Radioaktivität and Elektronik., 2, p. 42, 1905.

[3] Abstract of a paper presented at the Chicago meeting of the Physical Society, December 1, 1906.

ficial layer of the Moon's substance is considerably cooled in shadow, deeper layers continue hot and are competent to restore by conduction the heat lost by radiation during the few hours that the eclipse lasts.

The superficial layers of rock form a sufficient protection to the deeper ones to produce a large accumulation of thermal energy at the surface of the sunlit Moon after many days of continuous sunshine. Simple reflection will not explain the quality of the lunar radiation, which can be shown to proceed necessarily from a body at a high temperature.

Heat of Dilution.[1]

By F. L. Bishop.

THE apparatus employed was especially designed to insure that the two liquids should be at the same temperature when mixed and to avoid the determination of the specific heat of the solution.

The two calorimeters were so designed that one was inside the other and the liquid of the outer completely surrounded the inner calorimeter. The inner one which was provided with vanes on the inside and outside was suspended and rotated at a constant rate thus agitating the liquids. The mixing was accomplished by having the bottom of the inner one removable and lowering the calorimeter so that the liquids would pass down through the inner up the outer and over the top of the inner calorimeter. The change of temperature thus produced was measured with two Beckman's one in each calorimeter.

A quantity of heat necessary to produce the same change of temperature under the exact conditions existing when the two liquids were mixed, was supplied by an electric current. The coil was placed in the outer calorimeter just below the inner one. The current was adjusted until the rate at which the temperature changed was the same as when the liquids were mixed.

The whole apparatus was placed in a double walled vessel and immersed in a constant temperature bath.

The preliminary results seem to indicate that the values for $NaNO_3$ NH_4NO_3 and $Ba(NO_3)_2$ are within certain limits represented by a linear function of the heat and concentration.

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society, December 1, 1906.

THE RELATION BETWEEN URANIUM AND RADIUM.[1]

BY HERBERT N. MCCOY AND W. H. ROSS.

ONE of us has shown[2] that the radioactivity of any uranium mineral, free from thorium, is directly proportional to its uranium content; and for equal uranium content that minerals are 4.15 times as active as the pure compounds. The value, 4.15, previously found, is subject to three errors: (1) On account of the insufficient ionization space of the electroscope used; (2) on account of the portion of the emanation spontaneously lost; (3) on account of the unequal absorption of the rays by the rims of the shallow vessels containing the active films. New determinations of the composition and activity of uranium minerals have now been made, with all conceivable precautions to insure accuracy. We now find the corrected ratio of the activity of a mineral to that of a pure uranium compound, of equal uranium content, to be 4.58. We have, in addition, compared the activity of a minute quantity of Ra, free from all its products, with the activity of a standard film of U_3O_8; and also the activity of the emanation from this quantity of radium with that of the emanation associated with a known amount of uranium in a mineral. It was found that the activity of a quantity of uranium is 1.87 times that of the equilibrium amount of radium. Radium plus the equilibrium amounts of the emanation, *A* and *C* is 5.64 times as active as radium alone.[3] If we assume that the activity of RaF is proportional to its range, this product is 1.10 times as active as radium. Therefore radium and its products are 6.74 times as active as radium. In consequence, a mineral containing the equilibrium amounts of uranium, radium and products should be 8.61 times as active as the radium, or 4.60 times as active as the uranium it contains. The value found directly is 4.58.

If radium is considered a transformation product of uranium, as these and other experiments indicate, and further if the range of the α particle of uranium is taken as approximately 3.5 cm., that of radium being also 3.5 cm., and if the activity is assumed proportional to the range,[4] for equilibrium amounts of genetically related bodies producing equal numbers of α particles, then since uranium is about twice as active as the equilibrium amount of radium, the former must produce two α particles for every one produced by the equilibrium amount of the latter. This

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society, December 1, 1906.

[2] Ber., *37*, 2,641, 1904; Phil. Mag., *11*, 176, 1906.

[3] Boltwood, Am. J. Sci., *21*, 409, 1906.

[4] Boltwood, loc. cit.

indicates either that each atom of uranium produces, upon disintegration, two α particles, or that there is an α ray product, not yet isolated, between U and UX.

KENT CHEMICAL LABORATORY,
UNIVERSITY OF CHICAGO,
November 23, 1906.

AN INANIMATE DEMON.[1]

BY ALBERT B. PORTER.

CLERK MAXWELL'S intelligent "demon" was created for the purpose of showing the second law of thermodynamics to be a purely statistical result of molecular motion. The following argument avoids the necessity of invoking an animate demon. Imagine a gas-filled non-conducting vessel to be divided into two compartments by means of a conducting partition. Let the partition be pierced by numerous holes of molecular dimensions closed by very light spring trapdoors all opening toward the first compartment. These doors will be opened by impact of the gaseous molecules, thus permitting passage of the molecules from the second compartment into the first, but preventing the passage of any molecules in the other direction. There will thus be an accumulation of gas in the first compartment, and a corresponding rise of pressure which may be utilized as external work by permitting the gas to flow back into the second compartment through a turbine or other pressure engine. Mechanical work would thus be obtained by continuously cooling the working gas far below the temperature of surrounding objects until the molecular momentum became too feeble to force the trapdoors. If the turbine were made to do its work wholly within the containing vessel, this work would all be eventually given back to the gas in the form of heat. The arrangement would then constitute (in the German terminology) a perpetual motion of the second class. If the gas vessel were made with conducting walls, the engine would be capable of utilizing uniformly diffused heat, and would thus be independent of a source and sink.

It is not difficult to imagine a molecular structure having the sort of unilateral porosity required of the partition, but experiment has failed to realize such a septum. The assumption of structure of this sort in certain animal membranes might go far toward explaining such puzzling physiological phenomena as the high thermodynamic efficiency of the animal machine.

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society, December 1, 1906.

ON MULTIPLE CROSSED GRATINGS.[1]

BY ALBERT B. PORTER.

THESE gratings are made by contact printing on bichromated gelatine. By making a half-exposure, then turning the original grating through a right angle and completing the exposure, one secures, on developing the plate, a grating consisting of two sets of lines crossing at right angles. By making a half-exposure of this crossed grating on a second plate, turning it through 45° and completing the exposure, one obtains a set of four gratings crossed at 45° on one film. Continuing this double printing, a succession of crossed gratings are secured having 8, 16, 32, 64, etc., sets of lines. There is of course some loss of intensity at each step, but much less than might be expected. Starting with a grating ruled with 3,000 lines to the inch, a multiple grating has been made in this way having 1,024 sets of lines, each 3,000 to the inch, crossing at symmetrical angles. A gas flame seen through this plate appears to be surrounded by a continuous halo, but around a distant arc lamp the individual spectra can be seen and counted. Under the microscope regularity of structure can be recognized in the films bearing fewer than 32 crossed gratings, but the films which bear from 32 to 1,024 crossed gratings merely show a mosaic of numberless short lines running in apparently random directions.

A METHOD FOR THE DETERMINATION OF ELECTROLYTIC RESISTANCE AND CAPACITY.[1]

BY A. HOYT TAYLOR.

FOR very low voltages a polarizing electrolyte behaves like a capacity in series with a resistance; with possibly a second resistance in parallel.

It is possible to build an A. C. bridge with three non-inductive arms, the fourth arm consisting of a capacity C in series with a resistance r_2 and an inductance L_1 of resistance r_4. The capacity plus r_2 must be shunted with a resistance r_1; the inductance must be shunted with a resistance r_3. Under these conditions a perfect telephonic balance may be obtained providing the following equations hold:

$$C = \frac{r_3^2 L}{(r_3 + r_4)^2 r_1^2}; \quad \frac{r_1^2}{r_3^2} = \frac{r_1 + r_2}{r_3 + r_4}; \quad R = r_1 + \frac{r_3 r_4}{r_3 + r_4}.$$

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society, December 1, 1906.

The last equation allows us to calculate r_1, since R is the non-inductive resistance in the third bridge arm, the proportional arms being equal.

The second equations allow us to calculate r_2, while the first one gives C.

An electrolyte, sulphuric acid and water, with platinum electrodes, when substituted for the combination $r_2 + C$ gives very satisfactory balances when the E.M.F. is not over a few tenths of a volt.

An Experimental Gyroscope for Quantitative Work.[1]

By Frederick E. Kester.

THE fundamental theory of gyroscopic action can be put into such simple form, and the problem is so interesting and so instructive, that it would seem desirable to introduce quantitative work upon a suitably designed piece of apparatus as a regular laboratory experiment in undergraduate courses. The piece described in this paper was designed with the idea in view of allowing all necessary measurements to be made with an accuracy such as to give a sense of reliance in the principle involved in the experiment.

What may be called normal conditions of gyroscopic action exist when the fly-wheel is set spinning and the axis which carries it is turned with constant angular velocity about a second axis perpendicular to the first; in order to maintain this double rotation it is necessary to exert a moment of force about a third axis which is perpendicular to the plane of the first two axes. The magnitude of the moment of force is $I \cdot \omega_1 \cdot \omega_2$, where I is the moment of inertia of the fly-wheel, ω_1 and ω_2 are

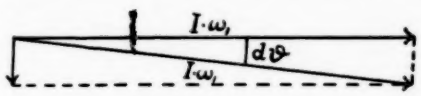

Fig. 1.

the angular velocities of the wheel and of its own axis about the second axis. If I be measured in g-cm.^{2} units and ω_1, ω_2 in radians per second, then the moment of force will be in cm.-dynes; if I be in lb.-ft.^{2}, the moment of force will be in poundal-ft.

In the piece under discussion the fly-wheel is carried on ball-bearings upon a horizontal spindle which is mounted at the end of a tube; the tube is, in reality, a balance beam and is provided with counterpoises on the end opposite the wheel. The balancing shaft (to take the place of the central knife-edge of the ordinary balance-beam) is also mounted on

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society, December 1, 1906.

balls; the bearings are at the tops of a vertical Y-piece, the lower end of which is long and constitutes the second axis mentioned above. The lower end of this vertical shaft carries a combination piece which is, essentially, a set of pulleys (graded in size) and a cylindrical surface about 20 cm. in diameter and 3 cm. high.

The laboratory experiment would involve the measurement of the two angular velocities and of the moment of force necessary to maintain equilibrium; from this data I is then calculated. The angular velocity of the wheel, ω_1, is determined from the clicking of a light spring at each revolution; that of the vertical shaft, ω_2 (a relatively slow motion) from the record, upon the cylindrical surface mentioned above, of a telegraph sounder which is beating seconds and which carries a scriber for tracing upon the whitened surface of the cylinder (a mixture of whiting and alcohol is very convenient here); divisions engraved upon the surface, at one edge, permit considerable accuracy in this measurement. A scale of millimeters along the side of the balance-beam together with the known mass of one of the counterpoises allow the measurement of the moment of force to be made with sufficient accuracy. Stops are provided for holding the balance-beam well within bounds, as is also a device for determining just when balancing conditions are attained.

The value of I thus obtained may be checked by calculation from the known mass and form of the wheel. The piece is so designed as to permit a second check on the value of I by the method described by Glazebrook and Shaw,[1] and by Millikan.[2]

[1] Practical Physics, 2d ed., p. 166.

[2] Molecular Physics and Mechanics, p. 81.